A Thesis

CRYSTAL-STRUCTURE STUDIES BY X-RAY AND NEUTRON DIFFRACTION

Submitted to the University of Glasgow for the Degree of Doctor of Philosophy in the Faculty of Science

by

Robert S. Dunlop, B.Sc.

Chemistry Department.

June 1973.

ProQuest Number: 11017936

All rights reserved

INFORMATION TO ALL USERS
The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript
and there are missing pages, these will be noted. Also, if material had to be removed,
a note will indicate the deletion.

ProQuest 11017936

Published by ProQuest LLC (2018). Copyright of the Dissertation is held by the Author.

All rights reserved.
This work is protected against unauthorized copying under Title 17, United States Code
Microform Edition © ProQuest LLC.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

TO

MY MOTHER AND FATHER

ACKNOWLEDGMENTS

I am grateful to Professor J.M.Robertson and to Professor G.A.Sim for providing the facilities for this work.

I should like to express my sincere thanks to Dr.J.C.Speakman for his encouragement and guidance throughout the period of these researches.

I am also indebted to Dr. J.G.Sime and Dr.D.D.MacNicol for their help and interest, and to Dr.H.H.Mills, under whose supervision the first parts of these researches were carried out.

I should like to thank the Science Research Council and the U.K.A.E.A. for making available to me neutron diffraction facilities at A.E.R.E. Harwell.

My thanks are also due to Dr.A.L.Macdonald and Dr.M.C.Currie for their help in collecting neutron diffraction data, and for the many valuable discussions I have had with them during the period of these researches.

Financial support from the Science Research Council is gratefully acknowledged.

SUMMARY

This thesis is concerned with the study of crystal structures by x-ray and neutron diffraction techniques, and also with the application of the symbolic addition method of solving crystal structures directly from the diffraction data.

Chapter 1 contains a review of direct methods of phase determination in diffraction experiments, the first part of the chapter being concerned with the historical background of the topic and the second part with the practical details of the symbolic addition method as applied to both x-ray and neutron diffraction data.

In Chapter 2, the crystal structure analysis of the stable free radical t-butylferrocenyl nitroxide is described, and the possibility of direct Fe...N or Fe...O bonding is discussed. The relative orientations of the two cyclopentadienyl rings are compared with the orientations of the cyclopentadienyl rings in other ferrocene derivatives, and the dimensions of the nitroxide radical are compared with those published for other nitroxide radicals.

Chapter 3 describes the refinement of the structure of the 1:1 complex of hexahelicene with 4-bromo-2,5,7-trinitrofluorenone, and the resulting dimensions of the hexahelicene molecule are compared with those predicted from molecular-orbital and valence-bond calculations in which a planar molecule was assumed.

In Chapter 4 the determination of the crystal structure of potassium tri-hydrogen di-succinate directly from neutron diffraction data is described and discussed; the refinement of the structure of potassium tri-hydrogen di-glutarate is described, and the structures of these 'super-acid' salts are discussed, in particular the dimensions of their hydrogen bonds.

Chapter 5 describes the x-ray and neutron diffraction analyses of the crystal structure of the neutral salt α-picoline N-oxide hydrochloride monohydrate, and the structure is described in terms of the disproportionation of a neutral salt into an acid salt and a basic salt. Particular attention is paid to the discussion of the 'acid salt' part of the structure, the bichloride ion $Cl\text{-}H\text{-}Cl^-$.

In Chapter 6, the structure analyses of the p-nitrosoaniline derivatives 9-nitrosojulolidine and N,N-diethyl p-nitrosoaniline are described, and the extent to which quinonoid-type structures contribute to the resonance hybrids of these compounds is discussed. The dimensions of their nitroso groups are discussed and compared with those of other nitroso compounds.

(The accuracy attained in the neutron analysis of the picoline salt was disappointing in relation to the chemical interest of this structure. It could have been improved had it been possible to use longer counting times.)

CONTENTS

CHAPTER 1

DIRECT METHODS OF PHASE DETERMINATION IN DIFFRACTION EXPERIMENTS

1.1. Introduction - The Phase Problem

When electromagnetic radiation falls upon matter it is scattered, and an image of the scatteringmatter may be constructed if the angular distribution of intensity, the frequency and phase of the scattered radiation is known. In mathematical terms, if the Fourier transform of an object is completely determined, the object itself is completely determined, and its form may be obtained by Fourier transformation.

When a beam of x-rays is incident upon a crystal, all the atoms in the path of the beam scatter coherently. In general, the scattered waves interfere with, and destroy one another, but in certain directions, dependent on the dimensions of the unit cell, they interfere constructively to form new wave fronts. This constructive interference is known as diffraction, and a crystal effectively behaves as a three-dimensional grating to x-rays. The resulting pattern of diffraction maxima is the Fourier transform of the unit cell contents sampled at specific points in reciprocal space - the reciprocal lattice points.

The values of the Fourier transform at these points - the structure factors - can be calculated for a structure of N atoms :

$$F_{\underline{h}} = |F_{\underline{h}}| e^{i\phi_{\underline{h}}} = \sum_{j=1}^{N} f_{j\underline{h}} \exp(2\pi i \underline{h} \cdot \underline{r}_j) \qquad (1.1)$$

where $F_{\underline{h}}$ is the structure factor associated with the reciprocal point of Miller indices (hkl), $\phi_{\underline{h}}$ is the phase associated with $F_{\underline{h}}$, $f_{j\underline{h}}$ is the atomic scattering factor of the j^{th} atom, and $r_j = (x_j, y_j, z_j)$ is a vector whose components are the co-ordinates of the j^{th} atom. The intensities of the

diffraction maxima are proportional to $F_{\underline{h}}^{2}$.

A more general form of equation (1.1) is :

$$F_{\underline{h}} = \int_{V} \rho(\underline{r}) \exp(2\pi i \underline{h}.\underline{r}) dr \qquad (1.2)$$

where $\rho(\underline{r})$ is the electron distribution function. $\rho(\underline{r})$ may be expressed in terms of $F_{\underline{h}}$ by means of the Fourier inversion theorem, giving :

$$\rho(\underline{r}) = \frac{1}{V} \sum_{-\infty}^{\infty} F_{\underline{h}} \exp(-2\pi i \underline{h}.\underline{r}) \qquad (1.3)$$

where V is the volume of the unit cell.

The electron distribution can thus be described by a Fourier series, the coefficients of which are the $F_{\underline{h}}$'s. The magnitudes of the $F_{\underline{h}}$'s can be readily derived from the intensities of the diffraction maxima, but there is no way of deriving experimentally the phases $\phi_{\underline{h}}$.

Thus the diffraction experiment does not provide sufficient data to enable the Fourier summation (1.3) to be carried out; the $\phi_{\underline{h}}$ must somehow be found before $\rho(\underline{r})$ can be calculated. This is the phase problem of crystallography.

1.2. Historical Background

In the early days of crystal-structure analysis, when trial and error methods alone were used in solving structures, it was a commonly-held belief that a direct solution to the phase problem was impossible in principle. Equation (1.3) seems to infer that for any given set of

structure amplitudes $F_{\underline{h}}$ there may be associated an arbitrary set of phases $\phi_{\underline{h}}$, each giving rise to an acceptable electron-density function $\rho(\underline{r})$. However, this argument overlooked the important restriction that $\rho(\underline{r})$ must be everywhere non-negative, and it was soon realised that a solution to the phase problem must exist, if only in principle.

The structure factor equations (1.1) form a system of simultaneous equations in which the phases $\phi_{\underline{h}}$ and the atomic positions $\underline{r}_j$ are the unknowns, and the $F_{\underline{h}}$ are known from experiment. Normally this system of equations is greatly overdetermined by the number of experimental data, so that it should be possible by algebraic means to solve for either the unknown phases $\phi_{\underline{h}}$ or the atomic positions $\underline{r}_j$. Since the equations (1.1) are not linear, simple elimination procedures cannot be used, and it would be an enormous computational task to attempt to solve such a set of equations for anything other than a trivial structure. However, the important point to emerge from the above argument was that the phases $\phi_{\underline{h}}$ (or the atomic positions $\underline{r}_j$) ought to be expressible in terms of the structure amplitudes $F_{\underline{h}}$.

The first attempt at deriving relationships between the structure amplitudes and atomic positions, by manipulating the structure factor equations, was by Ott[1] in 1928. His results were extended by Banerjee[2] to a routine for finding the signs of the structure factors, but the procedure was ineffective for all but the simplest structures.

An alternative and more rewarding approach to the phase problem was adopted by A.L. Patterson[3,4] in 1934 who investigated the properties of the

transform of the diffracted intensity distribution. The intensity I at any point in reciprocal space is proportional to the square of the structure amplitude ($F_{\underline{h}}$) at that point. Since $F_{\underline{h}}$ is a complex quantity, we have :

$$I \propto F_{\underline{h}} \cdot F_{\underline{h}}^{*} \qquad (2.1)$$

where $F_{\underline{h}}^{*}$ is the complex conjugate of $F_{\underline{h}}$. The transform of this product is, by the convolution theorem, the convolution of the transform of $F_{\underline{h}}$ (the electron density) with the transform of $F_{\underline{h}}^{*}$ (the electron density inverted at the origin), and can be represented as a Fourier series with the intensities as Fourier coefficients :

$$P(\underline{r}) = \sum I_{\underline{h}} \exp(-2\pi i \underline{h} \cdot \underline{r}) \qquad (2.2)$$

The maxima of this function (the Patterson function) represent the interatomic vectors from which it is possible tc determine the atomic positions.

Although a great many structures have been solved with the help of the Patterson function, the more complex ones with the aid of heavy atom substituents in the crystal, no general method of solution has so far resulted. The Patterson function of a structure containing only a moderate number of light atoms tends to have many overlapping peaks, and without some previous knowledge of the structure, interpretation may be very difficult. However, the relative success of the Patterson function did demonstrate that it was possible to extract phase information from a set of phaseless amplitudes, and stimulated a new search for relationships

between structure factors and phases.

In 1948 Harker and Kasper[5] derived inequality relationshiips between the structure factors, which depended on the positivity of the electron density. To do this, they made use of Cauchy's inequality, which may be written :

$$\left| \sum_{j=1}^{N} a_j b_j \right|^2 \leq \left(\sum_{j=1}^{N} |a_j|^2 \right)\left(\sum_{j=1}^{N} |b_j|^2 \right) \qquad (2.3)$$

where the a_j's and b_j's may be real or complex quantities. In dealing with inequalities, it was found convenient to define a normalised structure factor, the unitary structure factor (U) which gives the structure factor as the fraction of its maximum possible value :

$$U_{\underline{h}} = \frac{F_{\underline{h}}}{\sum_{j=1}^{N} f_j} = \sum_{j=1}^{N} n_j \exp 2\pi i \underline{h}.\underline{r}_j \qquad (2.4)$$

where $n_j = f_j \Big/ \sum_{j=1}^{N} f_j$

$U_{\underline{h}}$ thus has a maximum value of 1.

If $\sqrt{n_j}$ is substituted for a_j, and $\sqrt{n_j}\exp 2\pi i \underline{h}.\underline{r}$ for b_j in equation (2.3) the resulting inequality is :

$$|U_{\underline{h}}|^2 \leq \left(\sum_{j=1}^{N} n_j \right)\left(\sum_{j=1}^{N} n_j \exp 2\pi i \underline{h}.\underline{r}^{\,2} \right) \qquad (2.5)$$

Since $|\exp 2\pi i \underline{h}.\underline{r}|^2 = 1$, equation (2.5) becomes

$$|U_{\underline{h}}|^2 \leq \left(\sum_{j=1}^{N} n_j \right)^2$$

or $$\left|U_{\underline{h}}\right|^2 \leq 1$$

Although this result is trivial, when Cauchy's inequality is applied to the structure factor equations for structures containing symmetry elements, more useful inequality relationships are found. When a centre is present, the unitary structure factor equation is :

$$U_{\underline{h}} = \sum_{j=1}^{N} n_j \cos 2\pi \underline{h}.\underline{r}_j \qquad (2.6)$$

and applying Cauchy's inequality we have :

$$U_{\underline{h}}^2 \leq \left(\sum_{j=1}^{N} n_j\right)\left(\sum_{j=1}^{N} n_j \cos^2 2\pi \underline{h}.\underline{r}_j\right) \qquad (2.7)$$

or $$U_{\underline{h}}^2 \leq \tfrac{1}{2}\sum_{j=1}^{N} n_j\left(1 + \cos 2\pi 2\underline{h}.\underline{r}_j\right) \qquad (2.8)$$

and thus $$U_{\underline{h}}^2 \leq \tfrac{1}{2}\left(1 + U_{2\underline{h}}\right) \qquad (2.9)$$

This inequality can be used to show that if $U_{\underline{h}}$ and $U_{2\underline{h}}$ are both sufficiently large, $U_{2\underline{h}}$ must be positive. Other inequalities may be found for other symmetry elements, and MacGillavry[6] published a group-theoretical derivation of Harker-Kasper inequalities which enabled their straightforward determination for any space group.

Karle and Hauptman[7] investigated the relations between the phases and magnitudes of a set of structure factors on a more general basis by deriving a complete set of inequalities on the basis of the non-negativity of the electron density. They showed that a necessary and sufficient condition for the electron density to be everywhere positive is :

$$\begin{vmatrix} F_{ooo} & F_{\underline{h}_1} & \cdots\cdots\cdots & F_{\underline{h}_n} \\ F_{\underline{h}_1} & F_{ooo} & F_{\underline{h}_1-\underline{h}_2} \cdots & F_{\underline{h}_1-\underline{h}_n} \\ F_{\underline{h}_n} & \cdots\cdots\cdots\cdots & & F_{ooo} \end{vmatrix} \geq 0 \qquad (2.10)$$

The complete set of inequalities, which include all the Harker-Kasper inequalities, may be expressed in terms of determinants of higher and higher order, and thus of increasing complexity. Only the simpler inequalities have therefore found practical application, but with increasing structural complexity, they cease to be restrictive.

Several structures were solved using inequalities, but they contained comparatively few atoms in the unit cell, and it would be a fair comment that any structure solvable by inequalities could also be solved by some other non-direct methods of phase determination. Nonetheless, it was from Harker-Kasper inequalities that all subsequent direct methods of phase determination were evolved.

Probably the most important single advance in direct methods was achieved by Sayre[8] who, by examining the relations between the F's of a structure containing fully resolved identical atoms and the F's of the same structure in which the atoms were replaced by squared atoms, derived equations inter-relating the structure factors. The electron density $\rho(\underline{r})$ and its square $\rho^2(\underline{r})$ may be expressed as :

$$\rho(\underline{r}) = \frac{1}{V}\sum_{\underline{h}} F_{\underline{h}} \exp(-2\pi i \underline{h}.\underline{r}) \qquad (2.11)$$

$$\rho(\underline{r}) = \frac{1}{V}\sum_{h} F_{h} \exp(-2\pi i \underline{h}.\underline{r})$$

where $F_{\underline{h}}/_{V}$ is the h^{th} Fourier coefficient,

$$\rho^2(\underline{r}) = \frac{1}{V}\Sigma G_{\underline{h}} \exp(-2\pi i \underline{h}.\underline{r}) \tag{2.12}$$

where $G_{\underline{h}}/_{V}$ is the h^{th} Fourier coefficient of the squared structure.

It can be shown that the Fourier coefficients of the squared structure may be found by the self-convolution of the Fourier coefficients of the original function. Thus :

$$\frac{1}{V}G_{\underline{h}} = \Sigma_{\underline{k}} \frac{1}{V^2} F_{\underline{k}} F_{\underline{h}-\underline{k}} \tag{2.13}$$

or

$$G_{\underline{h}} = \frac{1}{V}\Sigma_{\underline{k}} F_{\underline{k}} F_{\underline{h}-\underline{k}} \tag{2.14}$$

Equation (2.14) relates the Fourier coefficients of the squared structure to those of the structure itself for a structure containing identical atoms.

If the atomic scattering factor of an atom is denoted by f and that of the squared atom by g, we have :

$$F_{\underline{h}} = \sum_{j=1}^{N} f \exp(2\pi i \underline{h}.\underline{r}) \tag{2.15}$$

and

$$G_{\underline{h}} = \sum_{j=1}^{N} g \exp(2\pi i \underline{h}.\underline{r}) \tag{2.16}$$

$$= \frac{g}{f} F_{\underline{h}} \tag{2.17}$$

Thus $$\frac{g}{f}F_{\underline{h}} = \frac{1}{V}\sum_{\underline{k}} F_{\underline{k}}F_{\underline{h}-\underline{k}} \qquad (2.18)$$

Equation (2.18) should be valid for a structure containing equal (or nearly equal) atoms, and was used successfully by Sayre to solve in two dimensions the structure of hydroxyproline. The direct application of Sayre's equation to determine signs is nevertheless too complex, especially in three dimensions, to be generally useful.

However, Zachariasen[9] (1952) and Cochran[10] (1952) were quick to notice that if the F's involved are sufficiently large, equation (2.18) can be simplified to:

$$F_{\underline{h}} \sim F_{\underline{k}}F_{\underline{h}-\underline{k}} \qquad (2.19)$$

As the magnitudes decrease in value, equation (2.19) will no longer be even approximately true, but it will still be probable that

$$sF_{\underline{h}} = sF_{\underline{k}}F_{\underline{h}-\underline{k}} \qquad (2.20)$$

or more generally

$$sF_{\underline{h}} = s\sum_{\underline{k}} F_{\underline{k}}F_{\underline{h}-\underline{k}} \qquad (2.21)$$

where s means 'sign of'.

Using a statistical approach, Cochran and Woolfson[11] derived an expression for the probability that the product $U_{\underline{k}}U_{\underline{h}-\underline{k}}$ gives a positive sign for $U_{\underline{h}}$:

$$P_{+}(\underline{h},\underline{k}) = \tfrac{1}{2} + \tfrac{1}{2}\tanh\left(\sigma_3/\sigma^3\right)\left|U_{\underline{h}}U_{\underline{k}}U_{\underline{h}-\underline{k}}\right| \qquad (2.22)$$

where $$\sigma_3 = \sum_{j=1}^{N} n_j^3$$

and $$\sigma = \sum_{j=1}^{N} n_j^2$$

For an equal atom structure, equation (2.22) becomes

$$P_+(\underline{h},\underline{k}) = \tfrac{1}{2} + \tfrac{1}{2}\tanh N\left|U_{\underline{h}} U_{\underline{k}} U_{\underline{h}-\underline{k}}\right| \qquad (2.23)$$

Although this simplified form of Sayre's relation (2.20), used in conjunction with the above probability expression, was a significant advance in the use of sign relationships, it could not be generally used without prior knowledge of the signs of some of the $F_{\underline{h}}$.

Karle and Hauptman[12] (1953) developed a statistical approach to the phase problem which yielded phase determining formulae in which phase information is deduced from the magnitudes of the structure factors. They noted that the probability of the sign of a structure factor being positive is one-half as long as no other intensities are known; once a set of intensities is known, the probability deviates from one-half. By a complex mathematical procedure, which involved integrating the atomic coordinates over all positions in the unit cell, they obtained a number of expressions similar in form to (2.22) for the probability that the sign of a structure factor is positive. They expressed their results in terms of the normalised structure factor defined as:

$$E_{\underline{h}} = \frac{U_{\underline{h}}}{\overline{U^2}^{\frac{1}{2}}} \qquad (2.24)$$

The first results, which are applicable to the space group $P\bar{1}$, may be expressed as :

$$\Sigma_1 : sE_{2\underline{h}} \sim s(E^2_{\underline{h}}-1) \qquad (2.25)$$

$$\Sigma_2 : sE_{\underline{h}} \sim s\sum_{\underline{k}} E_{\underline{k}} E_{\underline{h}-\underline{k}} \qquad (2.26)$$

$$\Sigma_3 : sE_{\underline{h}} \sim s\sum_{\underline{k}} E_{\underline{k}} (E^2_{(\underline{h}+\underline{k})/2} -1) \qquad (2.27)$$

$$\Sigma_4 : sE_{\underline{h}} \sim s\sum_{\underline{k}} (E^2_{\underline{k}} -1)(E^2_{\underline{h}-\underline{k}} -1) \qquad (2.28)$$

If symmetry other than a centre is present then stronger sign-determining formulae result. For example in the space group P_{2_1}/c an additional Σ_1 type formula may be derived :

$$sE_{2h02l} \sim s\sum_{\underline{k}} (-1)^{h+1} (E^2_{hkl} -1) \qquad (2.29)$$

Since only the magnitudes of the E's are known initially, Σ_1 or Σ_4 must be used to initiate the phase determination. Once sufficient signs have been determined, Σ_2, which is the same as Sayre's relationship, can be used to determine further signs. Although Karle and Hauptman used this method to solve several structures, it was not always successful, the main difficulty being the unreliability of Σ_1 and Σ_4. The reasons for this were pointed out by Vand and Pepinsky[13] (1953) and Bullough and Cruickshank[14] (1954). If the signs of the E's are controlled entirely by Σ_1, this is equivalent to computing a Fourier synthesis using $(E^2_{\underline{h}}-1)$ as coefficients - essentially a sharpened Patterson map with the origin removed, and the solution, using this as a start, tends to converge on the high peaks of the Patterson map. In the same way, using Σ_4, the solution converges on the high peaks of a map of the square of the Patterson density.

In recognition of the inadequacies of Σ_1 and Σ_4, and in the light of their own experiences with direct methods, Karle and Karle[15] in 1963 introduced the symbolic addition method of phase determination. Instead of first determining a basic set of signs using relationships such as Σ_1 and Σ_4, and then proceeding with Σ_2 using this basic set, the phase determining procedure is initiated and carried out in terms of a small properly chosen set of specified signs and unknown symbols using only the Σ_2 relationship. If x symbols are used, then in principle 2^x Fourier maps must be computed, in order to find the correct solution, although relations are usually found between the unknown symbols which reduce this number. As well as being both simple and reliable, the symbolic addition method has the advantage of being easily carried out by hand, and is now probably the most widely used method of direct phase determination.

So far, only the case of the centrosymmetric space groups has been discussed; in its more general form,[12] Karle and Hauptman's theory can be extended to deal with non-centrosymmetric space-groups. Phase determination in this case is initiated using a formula similar to Σ_2. If one has three structure factors of indices $\underline{h}$, $\underline{k}$, and $\underline{h}-\underline{k}$, the expected value of the phase $\phi_{\underline{h}}$ is given by :

$$\phi_{\underline{h}} \approx \langle \phi_{\underline{k}} + \phi_{\underline{h}-\underline{k}} \rangle_{k_r} \qquad (2.30)$$

Approximate phases for additional E's can then be calculated using the tangent formula :

$$\tan\phi = \frac{\sum_{\underline{k}} E_{\underline{k}} E_{\underline{h}-\underline{k}} \sin(\phi_{\underline{k}} + \phi_{\underline{h}-\underline{k}})}{\sum_{\underline{k}} E_{\underline{k}} E_{\underline{h}-\underline{k}} \cos(\phi_{\underline{k}} + \phi_{\underline{h}-\underline{k}})} \qquad (2.31)$$

1.3. The Symbolic Addition Method of Direct Phase Determination for Centrosymmetric Crystal Structures

(a) Preparation of normalised structure factors

The observed structure factors (F_{obs}) are first put on an absolute scale and corrected for thermal motion using either a Wilson plot or K-curve.

Wilson[16] pointed out that for absolute intensities

$$\langle I_h \rangle = \sum_j f_j^2 = \sigma \qquad (3.1)$$

and that the observed intensities, I_{hobs} will differ from the I_h by a scale factor k, independent of θ, and a temperature factor. Thus, if we assume a temperature factor of the form $\exp(-Bs^2)$, were $s = \sin\theta/\lambda$, we have :

$$I_{\underline{h}obs} = kI_{\underline{h}}\exp(-Bs^2)$$

The reflections can be divided into groups covering different ranges of s, and within each group the ratios :

$$\frac{\Sigma\sigma}{I\,\underline{h}obs} \quad \text{or} \quad \frac{\Sigma\sigma}{F^2\,\underline{h}obs} = r \qquad (3.2)$$

are computed. A plot of log(r) vs. s^2 at the average value of s^2 within each group should thus give a straight line of slope B and inter-

cept - log k. This is known as a Wilson plot.

Alternatively, if (3.2) is plotted directly as a function of s at the average value of s within each group, without assuming a form for the temperature factor, the resulting curve will have an intercept $^1/_k$ when s = 0, and the shape of the curve will give the statistical temperature correction, which need not be Gaussian; this is the k-curve.

Having put the observed structure factors on an absolute scale and corrected them for vibrational motion using either of the above methods, the normalised structure factors are calculated according to equation :

$$E_{\underline{h}}^{\,2} = \frac{F_{\underline{h}}^{\,2}}{\varepsilon \sum_j f_j^{\,2}}$$

where $F_{\underline{h}}$ is the corrected structure factor magnitude, f_j is the j^{th} atomic scattering factor for the j^{th} atom in a unit cell containing N atoms, and ε is a number which corrects for space group extinctions.

The normalised data are then separated into eight subgroups according to the parity of their Miller indices, and listed in order of decreasing |E|. Those E's above a certain arbitrary value, usually $|E| \geq 1.5$, are then used to generate all the possible 'triples' $\underline{h}$, $\underline{k}$, $\underline{h}-\underline{k}$ for use with Σ_2. For each triple, the probability that

$$s(\underline{h}).s(\underline{k}).s(\underline{h}-\underline{k}) = +1 \qquad (3.3)$$

is evaluated, assuming an equal, or nearly equal atom structure, using a formula derived from equation (2.22)

$$P_+ = \tfrac{1}{2} + \tfrac{1}{2}\tanh \frac{1}{\sqrt{N}}\left|E_{\underline{h}} \cdot E_{\underline{k}} \cdot E_{\underline{h}-\underline{k}}\right| \qquad (3.4)$$

(b) Specification of an origin

The first step in the phase determining procedure is to define an origin, since the values of the phases depend, in general, not only on the structure, but also on the choice of origin. For the centrosymmetric space groups, the permissible origins are the eight centres of symmetry in the primitive unit cell. Usually the eight centres are not equivalent, since different centres may be situated differently with respect to the various symmetry elements. As a result, phases may be divided into two classes: those which change sign with a change in origin - structure seminvariants, and those which depend solely on the structure - structure invariants.

The centrosymmetric space groups may have one, two, four or eight classes of equivalent origins and it is then necessary to assign the values of three, two, one or zero appropriate phases, respectively, in order to specify the origin.

The theory of structure seminvariants has been worked out in detail for all the space groups; tables[17,18,19,20] are given which divide the space groups into types according to the nature of their equivalent sets of permissible origins. Within each type of space group, the invarient and seminvarient phases are listed, as well as the number of phases which require to be assigned in order to define an origin. For example, in

the primitive centrosymmetric space groups of the triclinic, monoclinic and orthorhombic classes (Type 1P), three phases require to be assigned in order to define an origin. Phases of reflections whose indices are all even (eee) are structure invarients in this type of space group and thus cannot be used to define an origin. Likewise, any linear combination of three phases whose indices add up to (eee) is also structure invariant; such phases are linearly dependent. Only combinations of three phases which are linearly independent can thus be used to define an origin. In making the phase assignments, the largest suitable $|E_{\underline{h}}|$ are used, the choice being partly determined by the extent to which a particular $\underline{h}$ enters into the Σ_2 triples.

(c) Determination of phases

Having specified an origin, one unknown symbol is then assigned to a suitable large $|E_{\underline{h}}|$ which is involved in many Σ_2 relationships. Equation (3.3) is then used to define as many signs of the largest $|E_{\underline{h}}|$ as possible, in terms of both the specified ones and others that have been newly determined. Additional symbols are assigned when required to other large $|E_{\underline{h}}|$ which enter into a large number of Σ_2 relationships. It is possible to proceed in this manner until the phases of all or most of the largest $|E_{\underline{h}}|$ are known in terms of the specified signs and unknown symbols.

As the phase determination proceeds, and relationships involving smaller $|E_{\underline{h}}|$ are employed, the probabilities determined from (3.4) will

decrease; that is, the relationships will become less reliable, and Karle and hauptman recommend that a relationship should be rejected if $P_+ < 0.97$. However, relationships with lower probabilities can usually be employed in the latter stages of phase determination, if necessary, in an attempt to gain more signs.

Usually no more than three or four unknown symbols are required during a determination, which means that, in theory, there will be 2^3 or 2^4 possible solutions respectively. Fortunately relationships between the unknown symbols often arise during the phase determination, in favourable circumstances providing a unique solution, and in less favourable circumstances leaving only two or four possible solutions. Other criteria, such as the relative number of positive and negative phases, also help in deciding which solutions are likely to be correct.

(d) Calculation of E-maps

Once one or more possible solutions have been determined, their validity is tested by calculating Fourier syntheses. It has been found more useful to calculate syntheses in which the coefficients are E's rather than F's. This is because a large number of the phased E's are derived from fairly high-order reflections which, although they have large $|E|$'s, have small values for $|F|$ which tend to be swamped in a Fourier synthesis by a few strong low-order F's.

'E-maps' are effectively sharpened Fourier maps, and nearly always contain too many peaks. Choosing a chemically sensible set of peaks is

usually fairly straightforward for most structures, but structures containing highly symmetrical features, such as several six-membered rings, sometimes give rise to E-maps which have several possible interpretations.

1.4. The Direct Determination of Phases from Neutron Data

Since neutron diffraction data are normally phased initially using the previously determined x-ray structure, a means of determining phases directly from a set of neutron structure amplitudes would be useful when x-ray data are not available, or when a heavy-atom structure determined by x-rays contains poorly resolved light atoms.

It was thought initially[21] that the methods applicable to x-ray data, in particular the symbolic addition method, are not directly applicable to neutron data, since certain atoms, notably hydrogen, have negative scattering factors for neutrons; x-ray scattering factors are always positive.

In deriving the sign relationship (2.20) from Sayre's equation (2.18) it was shown that the phases and magnitudes of the original and squared structures are the same for the largest normalised structure amplitudes. In the case of neutron diffraction, where some atoms may be scattering with negative scattering factors, the phases and magnitudes of the normalised structure factors for the squared structure may be different from those of the original structure, making the use of equation (2.20) invalid.

Karle[21] suggested that if the structure amplitudes expected from the squared structure could be calculated from the observed amplitudes,

the conventional symbolic addition procedure could then be applied, since all the atoms would have positive scattering factors as in the case of x-ray diffraction. This would lead to the squared structure from which the original structure could be derived; the structure of glycolic acid has been solved directly from neutron data by Ellison and Levy[22] using this 'squared structure' method.

However, it is likely that the glycolic acid structure could, in fact, have been solved by the conventional symbolic addition method. To see why this is so, let us look more closely at the effect of negative scattering hydrogen nuclei on the structure factors obtained from a typical organic crystal by neutron diffraction. The nuclear scattering lengths ($\bar{b}$) of carbon, oxygen and hydrogen are 0.661, 0.577 and -0.378 $\times 10^{-12}$ cms. respectively. Their respective scattering powers are thus in the ratio of $0.661^2 : 0.577^2 : (0.378)^2$ or 0.44:0.34: 0.14 - roughly 3:2:1 compared with 36:64:1 for x-rays. It can be seen, therefore, that the 'heavy elements' carbon and oxygen are still the dominant scatterers, though to the extent of an order of magnitude less than for x-rays. The differences in the neutron structure factors of an organic structure containing a moderate proportion of negatively scattering hydrogens and the same structure in which the hydrogens scatter positively can thus be predicted as :

(a) proportionately large differences in amplitude among a number of the weaker F's; many may also have different signs.

(b) proportionately small differences in amplitude among the

largest F's, and no difference in sign.

Thus, although the phases of some of the structure factors for the squaredstructure may differ from those of the original structure, the important point is that, as long as there is only a moderate proportion of hydrogens in the structure, the phases of largest structure factors will be the same in the original and squared structures.

Also, since the nuclear scattering length, $\bar{b}$, does not change with increasing Bragg angle θ , it is generally the case with neutron data that large E's correspond to large F's, so that the phases of the largest E's will be the same in the original and squared structures, and it should therefore be permissible to proceed with phase determination using the conventional symbolic addition method. It has been suggested[18] that the symbolic addition method may be used with neutron data when the scattering due to hydrogen is less than $\frac{1}{3}$ of the total scattering :

$$\sum_H b_H^2 \Big/ \sum_{\substack{\text{all} \\ \text{atoms}}} b_j^2 < \tfrac{1}{3}$$

That the symbolic addition method can be successfully applied to neutron data is demonstrated in Chapter 4 where the determinations of the structures of potassium trihydrogen disuccinate and potassium trihydrogen diglutarate are described; the proportion of negative scattering power in these structures is 20% and 22% respectively. The first non-centrosymmetric structure to be solved directly from neutron data - L-proline monohydrate - has been reported[18] by Verbist et al, and they conclude that

'direct methods can probably be applied to neutron diffraction data for almost any crystal to which they are applicable to x-ray diffration data'.

References

1. H. Ott, Z. für Krist., 66, 136 (1928).

2. K. Banerjee, Proc. Roy. Soc. A, 141, 188 (1933).

3. A.L. Patterson, Phys. Rev., 46, 372 (1934).

4. A.L. Patterson, Z. für Krist., 90, 517 (1935).

5. D. Harker and J.S. Kasper, Acta Cryst., 1, 70 (1948).

6. C. MacGillavry, Acta Cryst., 3, 214 (1950).

7. J. Karle and H. Hauptman, Acta Cryst., 3, 181 (1950).

8. D. Sayre, Acta Cryst., 5, 60 (1952).

9. W.H. Zachariasen, Acta Cryst., 5, 68 (1952).

10. W. Cochran, Acta Cryst., 5, 65 (1952).

11. W. Cochran and M.M. Woolfson, Acta Cryst., 8, 1 (1955).

12. H. Hauptman and J. Karle, Solution of the Phase Problem. I. A.C.A. Monograph No. 3. New York (1953).

13. V. Vand and R. Pepinsky, X-ray and Crystal Analysis Laboratory, Dept. of Physics, Pennsylvania State University, 1-98 (1953).

14. R.K. Bullough and D.W.J. Cruickshank, Acta Cryst., 7, (1954).

15. I.L. Karle and J. Karle, Acta Cryst., 16, 969 (1963).

16. J. Karle, Acta Cryst., 20, 881 (1966).

17. R.D. Ellison and H.A. Levy, Chem. Div. Ann. Prog. Report, ORNL-4164, 126.

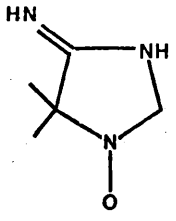
18. Verbist, Lehmann, Koetyle and Hamilton, Nature, 235, 328 (1972).

CHAPTER 2

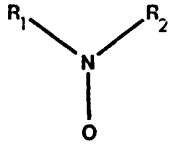
THE CRYSTAL AND MOLECULAR STRUCTURE OF t-BUTYLFERROCENYL NITROXIDE

2.1. Introduction

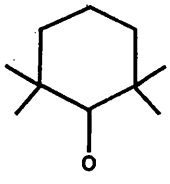
The first stable organic nitroxide radical, porphyrexide (I), was isolated and characterised by Piloty and Schwerin[1] in 1901; during the years 1912-22 Wieland[2] prepared a number of relatively stable diaryl nitroxides of type (II), with R_1 and R_2 = aryl, and in 1959 Lebedev and Kazarnovski[3] succeeded in isolating the first completely aliphatic nitroxide radical (III).



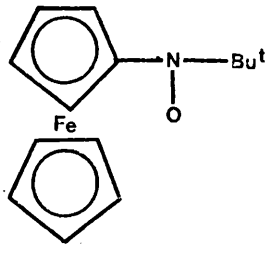
I



II



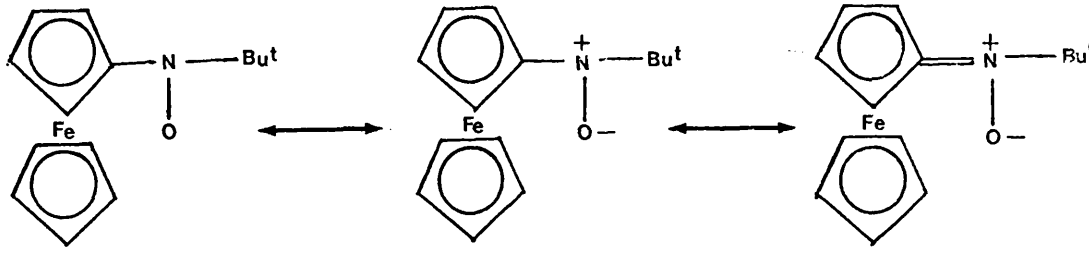
III



IV

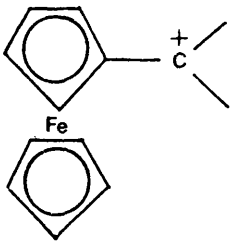
This was followed shortly afterwards by Hoffmann's synthesis[4] of di-t-butyl nitroxide. The rapid development of e.s.r. spectroscopy in recent years has stimulated a renewed interest in nitroxide radicals, and a large number have been synthesised and examined. t-Butylferrocenyl nitroxide (IV), believed to be the first stable, neutral ferrocenyl radical to be isolated,[5] is of particular interest. Its e.s.r. spectrum

(Figure 2.1) has some unusual features - an a_N value of 11.75 G which is similar to that found in aryl-t-butyl nitroxides (about 12.0 G) but a g-value of 2.0149 $\pm$ 0.0004 which is much larger than the normal value for aryl-t-butyl nitroxides (about 2.006). The smaller coupling (0.8G) in the spectrum, which almost certainly arises from the 2- and 5-ring protons, is less than half that of the ortho-protons in aryl-t-butyl nitroxides (a_{O-H} ca. 2.0 G). These results indicate that the unpaired electron is extensively delocalised and that there is considerable interaction with the iron atom. This could occur either via the metal-ring π-system ($IV_a \longleftrightarrow IV_b \longleftrightarrow IV_c$).



IV_a IV_b IV_c

and/or by direct Fe-N (or O) bonding - direct bonding between electron-deficient carbon and iron has frequently been invoked[6] to explain the unusual stability of α-ferrocenylcarbonium ions (V).



V

The structure of t-butylferrocenylnitroxide was thus determined in order to examine the possibility of direct bonding, and also to determine the bond lengths and angles of the nitroxide moiety.

2.2. Experimental

The crystals of t-butylferrocenyl nitroxide were deep-red in colour and needle-shaped, with the needle axis along the a-direction. The unit-cell dimensions and space-group were determined from rotation, Weissenberg and precession photographs taken with a crystal mounted along its needle axis. Cu-K_α radiation of wavelength 1.5418 Å was used.

Crystal Data

$C_{14}H_{18}NOFe$, M = 272.14. Monoclinic, $\underline{a}$ = 5.90 (1), $\underline{b}$ = 15.71 (2), $\underline{c}$ = 14.38 (2) Å, β = 109.25 (0.25)°. $\underline{U}$ = 1258.2 Å^3, $\underline{D}_m$ = 1.42, $\underline{z}$ = 4, $\underline{D}_c$ = 1.43. μ(Cu-K$_\alpha$) = 96.57 cm^{-1}. Space group $P2_1/c$ (No. 14).

Data Collection

Intensities were estimated visually from equi-inclination Weissenberg

photographs (using Cu-K_α radiation) of reciprocal-lattice nets 0kl - 5kl. A crystal of dimensions 1.0 x 0.25 x 0.15 m m^3 mounted along its needle axis was used, and 1,237 independent intensities were measured which were significantly above background. Lorentz and polarisation corrections were applied to the data, but no absorption corrections were applied.

2.3. Structure Determination and Refinement

The structure was solved by the heavy-atom method. The coordinates of the iron atom were determined from a three-dimensional Patterson synthesis, and the signs of the structure factors obtained from the iron contributions were used in computing an electron-density map in which all the remaining sixteen atoms in the molecule were clearly resolved. Structure factors based on all seventeen atoms gave an R value of 29.0%.

Using unit weights, three cycles of full-matrix least-squares refinement of positional and isotropic temperature factors, and batch scale factors, reduced R to 17.3%. A further four cycles of block-diagonal refinement with anisotropic temperature factors and an overall scale factor, completed the refinement, and reduced R to 9.3% with $R' \left(\Sigma W\Delta^2/\Sigma WF_o^2\right) = 1.6\%$. The weighting scheme used in the final three cycles is represented by the equation :

$$W = \left\{\left[1-\exp(-p_1(\sin\theta/\lambda)^2\right]/\left[1 + p_2|F_c| + p_3|F_c|^2\right]\right\}$$

The final values for the three parameters were $p_1 = 20$, $p_2 = 0.0001$,

p_3 = 0.0005. The scattering factor curves used for Fe, C, N, and O were those from International Tables for Crystallography (1962).

The values for the atomic coordinates and vibrational parameters are given in Tables 2.1 and 2.2 respectively, and the observed structure amplitudes and calculated structure factors are listed in Table 2.3.

2.4 Discussion of the Structure

The structure and numbering scheme of t-butylferrocenylnitroxide is shown in Figure2.2, and the bond lengths and angles are given in Table 2.4.

The N-O bond length is 1.263 (15) Å, which is intermediate between that of an N-O double bond (1.20 Å)[7] and an N-O single bond (1.44 Å).[7] This is consistent with the three-electron nitroxide N-O bond postulated by Hoffmann and Henderson,[4] and later by Linnet[8] in his double-quartet theory of bonding.

The atoms C(1), N, C(11) and O are coplanar; the mean plane through them is represented by the equation $-0.5947\,X' + 0.7016\,Y + -0.3925\,Z' = 3.2126$ Å, (the root mean square distance of the four atoms from the plane is 0.005 Å) and makes an angle of only 13.1° with the cyclopentadienyl ring. The Fe....N and Fe....O distances are 3.112 (9) and 3.629 (11) Å respectively, while the C (1) - N distance is 1.393 (14) Å, considerably less than the accepted C-N single bond length of 1.47 Å. These results indicate that direct Fe - N or Fe - O bonding, if any, must be weak, and the radical thus resembles more closely models

of the α-ferrocenylcarbonium ion[9] in which electron delocalisation occurs mainly via the metal-ring π-system.

The structural parameters of several other nitroxides have been determined by x-ray or electron-diffraction techniques, and the relevant bond lengths and angles from these structures (which are labelled 1 to 7) are summarised in Table 2.5. With the exception of di-p-anisylnitroxide (3), which was solved in projection, the values for the N-O distances agree within the limits of experimental error (mean value 1.278 ± 0.008 Å) and apart from di-t-butylnitroxide (2) and the two five-membered ring structures (5 and 7), the C-N-C angles are also remarkably constant (mean value 123.3 ± 0.9°). In di-t-butyl nitroxide, the bulky t-butyl groups are probably causing a widening of the bond angle in an effort to reduce non-bonded interactions, while in structures 5 and 7, the ring size probably prevents any widening of the C-N-C angle. The dihedral angle which the N-O bond subtends with the C-N-C plane varies from 0° (planar) to 24° (pyramidal). However, examination of the non-bonded distances suggests[10] that steric factors determine the deviation from planarity; in all cases except di-p-anisyl nitroxide the oxygen makes close O····C contacts, or a close O····F contact , in the case of structure (1). In t-butylferrocenylnitroxide and di-p-arisyl nitroxide, π-delocalisation over the N-O bond and aromatic system is probably the major factor in achieving planarity. The geometry of the nitroxide radical thus seems to be fairly well defined by the structures so far determined: in the absence of any steric effects, it has a planar

nitrogen, with an N-O distance ca. 1.28 Å and a C-N-C angle ca. 123°. Given the accuracy of the results in Table 2.5, it is not really valid to assess the effects of different substituents on the N-O bond length, but they do suggest that any system into which the lone electron can be delocalised will cause a slight increase in the double-bond character of the N-O bond, as would be expected.

In the ferrocenyl residue, the iron atom is symmetrically placed between eclipsed cyclopentadienyl rings, with an average Fe····C distance of 2.038 ± 0.007 Å. The average C-C distance in the cyclopentadienyl rings is 1.400 ± 0.011 Å, and the average internal ring angle 107.99 ± 1.1°. These values agree well with those of other recently-determined structures of ferrocene derivatives.[17,18,19,20,21,22,23]

The mean plane through the substituted cyclopentadienyl ring is defined by the equation $-0.3985\,X' + 0.8172\,Y - 0.4165\,Z' = 3.9346$ Å, and the root mean square distance of the atoms from the plane is 0.014 Å. The equation of the mean plane through the unsubstituted cyclopentadienyl ring is $-0.4197\,X' + 0.8037\,Y - 0.4219\,Z' = 0.5533$ Å while the root mean square distance of the atoms from the plane is 0.003 Å. The dihedral angle between the two rings is 1.47°, which means that they are coplanar within the limits of experimental error; the perpendicular distance between the rings is 3.31 Å. A point of interest in ferrocene derivatives is the conformation of the two cyclopentadienyl rings. In the case of t-butylferrocenylnitroxide they are eclipsed; in other ferrocenes they vary from being fully eclipsed to the fully staggered. However, as

more ferrocene structures are solved, it is becoming apparent that the majority of ferrocenes are nearer the eclipsed than the staggered conformation. This is consistent with electron diffraction results[24,25] which show that the free ferrocene molecule is eclipsed with a barrier to rotation of 0.9 k.cal.mole^{-1}; thus while crystal packing forces will be the major factor in influencing the conformations in ferrocenes, there will be a tendency to favour the eclipsed conformation where possible.

References

1. O. Piloty and B.G. Schwerin, Ber., 34, 1870 (1901).
2. H. Wieland and F. Kőzl, Ber., 55, 1798 (1922).
3. O.L. Lebedev and S.N. Kazarnovskii, Papers on Chemistry and Chemical Technology, Gor'kii, 2, 649 (1959).
4. A.K. Hoffmann and A.T. Henderson, J. Amer. Chem. Soc., 83, 4671 (1961).
5. A.R. Forrester, S.P. Hepburn, R.S. Dunlop and H.H. Mills, Chem. Comm., 699 (1969).
6. M. Cais, Organometallic Chem. Rev., 1, 435 (1966).
7. L. Pauling, 'The Nature of the Chemical Bond', Cornell University Press, (1960).
8. J W Linnet, 'The electronic structure of molecules' Methuen, (1966)
9. J.G. Taylor and J.C. Ware, J. Amer. Chem. Soc., 89, 2304 (1967).
10. C. Glidewell, D.W.H. Rankin, A.G. Pobiette, G.M. Sheldrick and S.M. Williamson, J. Chem. Soc. (A), 478 (1971).
11. B. Andersen and P. Andersen, Acta Chem. Scand., 20, 2728 (1966).
12. A.W. Hanson, Acta Cryst., 6, 32 (1953).
13. L.J. Berliner, Acta Cryst., B26, 1198 (1970).
14. J.C.A. Boeyens and G.J. Kruger, Acta Cryst., B26, 668 (1970).
15. D.M. Hawley, G. Ferguson and J.M. Robertson, J. Chem. Soc. (B), 1225 (1968).
16. W. Turley and F. Peter Boer, Acta Cryst., B28, 1641 (1972).

17. M.R. Churchill and J. Wornald, Inorg. Chem., 8, 716 (1969).

18. K. Hirotou, T.Higuchi, and A. Shirneda, Bull. Chem. Soc., Japan, 41, 1557 (1968).

19. G.J. Palenik, Inorg. Chem., 8, 2744, (1969).

20. G.J. Palenik, Inorg, Chem., 9, 2424 (1970).

21. H.L. Halland and G.M. Brown, Acta Cryst., B27, 81 (1971).

22. F.H. Allen, J. Trotter and C.S. Williston, J. Chem. Soc. (A), 907 (1970).

23. A.P. Krukonis, J. Silverman and N.F. Yannoni, Acta Cryst., B28, 987 (1972).

24. R.K. Bohn and A. Haaland, J. Organometallic Chem., 5, 470 (1966).

25. A. Haaland and J.E. Nilsson, Chem. Comm., 88 (1968).

TABLES AND DIAGRAMS

Table 2.1

Fractional coordinates (x, y, z) and absolute orthogonal coordinates (in Å with $X' = ax\sin\beta$, $Y = by$, $Z' = cz\cos\beta + ax$, and with standard deviations in parentheses).

	x	y	z	X'	Y	Z'
Fe	0.2559	0.2165	0.219	1.425(2)	3.402(2)	-0.183(2)
O	-0.0737	0.3468	0.1420	-0.411(11)	5.449(12)	2.185(11)
N	0.0978	0.3742	0.1162	0.544(10)	5.880(9)	1.480(10)
C(1)	0.1248	0.3367	0.0327	0.695(9)	5.291(10)	0.227(11)
C(2)	0.3198	0.3381	-0.0060	1.781(12)	5.313(14)	-0.708(12)
C(3)	0.2528	0.2911	-0.0918	1.408(15)	4.573(12)	-1.811(11)
C(4)	0.0237	0.2587	-0.1106	0.132(14)	4.064(12)	-1.637(14)
C(5)	-0.0605	0.2829	-0.0330	-0.337(12)	4.444(13)	-0.357(14)
C(6)	0.3828	0.1656	0.1572	2.132(18)	2.602(16)	1.516(13)
C(7)	0.5724	0.1693	0.1188	3.188(13)	2.660(14)	0.595(12)
C(8)	0.4930	0.1194	0.0334	2.745(15)	1.876(13)	-0.479(15)
C(9)	0.2731	0.0866	0.0210	1.521(15)	1.361(14)	-0.229(17)
C(10)	0.2007	0.1156	0.0996	1.118(16)	1.817(14)	1.041(18)
C(11)	0.2586	0.4421	0.1781	1.440(12)	6.946(13)	2.058(12)
C(12)	0.3294	0.5046	0.1171	1.835(17)	7.929(13)	1.043(16)
C(13)	0.1180	0.4845	0.2346	0.657(20)	7.612(20)	3.144(21)
C(14)	0.4858	0.3966	0.2489	2.706(16)	6.231(15)	2.633(16)

Table 2.2

Anisotropic temperature parameters (Uij in $\mathring{A}^2$ x 10^3) with standard deviations in parentheses.

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Fe	38(1)	30(1)	37(1)	2(2)	38(1)	5(2)
O	82(7)	99(8)	124(9)	-101(14)	157(14)	-81(12)
N	58(6)	36(5)	60(6)	-34(9)	67(10)	-12(8)
C(1)	31(5)	37(6)	39(6)	11(9)	11(9)	6(8)
C(2)	47(7)	71(9)	63(8)	25(13)	78(13)	27(12)
C(3)	99(10)	50(7)	35(6)	-12(11)	59(13)	25(14)
C(4)	68(9)	41(7)	57(8)	-22(11)	30(13)	11(11)
C(5)	43(7)	54(7)	68(8)	-28(13)	11(11)	8(12)
C(6)	120(13)	76(10)	52(8)	61(15)	110(18)	87(19)
C(7)	60(8)	63(8)	43(7)	20(12)	16(12)	49(13)
C(8)	69(9)	53(8)	72(9)	24(14)	60(15)	41(13)
C(9)	74(10)	52(7)	90(10)	44(15)	53(16)	6(14)
C(10)	81(10)	42(7)	130(14)	44(16)	120(20)	-4(14)
C(11)	46(7)	57(7)	51(7)	-35(11)	42(11)	-16(11)
C(12)	109(12)	35(7)	65(10)	15(12)	18(17)	-28(14)
C(13)	114(14)	99(14)	151(18)	-186(27)	168(27)	-101(22)
C(14)	83(10)	56(8)	70(9)	32(14)	31(15)	4(14)

Table 2.3

Observed structure amplitudes and final calculated structure factors.

H	K	L	F OBS	F CALC
0	4	0	11.0	-8.3
0	6	0	19.9	13.3
0	8	0	20.4	21.6
0	10	0	28.2	26.3
0	12	0	22.4	-22.4
0	14	0	29.2	29.1
0	16	0	23.1	-20.8
0	18	0	23.2	24.6
0	2	1	23.3	16.5
0	7	1	78.7	-71.4
0	8	1	20.3	18.9
0	9	1	52.8	49.6
0	11	1	20.3	-17.5
0	3	2	71.4	-73.4
0	4	2	24.2	25.0
0	5	2	76.2	70.0
0	6	2	24.8	-20.9
0	7	2	10.5	-7.7
0	10	2	27.8	23.5
0	12	2	27.2	-28.4
0	14	2	27.4	30.4
0	16	2	22.9	-24.5
0	16	2	14.6	15.2
0	1	3	55.9	58.4
0	2	3	59.2	-62.7
0	4	3	21.1	20.5
0	5	3	18.3	21.2
0	6	3	51.4	-47.5
0	7	3	55.8	-56.0
0	8	3	50.8	47.1
0	9	3	64.9	64.9
0	10	3	23.5	-26.1
0	11	3	29.9	-31.0
0	14	3	8.7	-7.7
0	15	3	13.1	12.2
0	1	4	21.5	-18.8
0	2	4	30.4	-34.7
0	3	4	11.0	-3.6
0	4	4	30.2	36.0
0	5	4	9.4	5.8
0	6	4	36.3	-37.6
0	7	4	28.7	24.5
0	8	4	21.3	-22.6
0	10	4	27.6	29.4
0	11	4	21.3	-19.5
0	12	4	21.2	-20.0
0	14	4	10.0	19.0
0	16	4	25.3	-28.5
0	1	5	19.8	14.2
0	2	5	22.2	-28.0
0	3	5	21.2	-20.9
0	4	5	27.4	24.8
0	5	5	34.9	33.9
0	6	5	30.8	-29.9
0	7	5	44.9	-45.9
0	8	5	47.7	44.7
0	9	5	59.3	58.9
0	10	5	33.2	-30.8
0	11	5	24.3	-23.1
0	12	5	20.9	21.1
0	1	6	38.7	-35.0
0	2	6	44.6	-42.5
0	3	6	40.7	36.6
0	4	6	9.9	10.9
0	5	6	48.0	-45.6
0	6	6	9.5	8.1
0	7	6	12.2	10.2
0	8	6	26.8	-26.8
0	9	6	16.3	14.4
0	10	6	8.2	-5.6
0	11	6	13.8	-13.5
0	12	6	10.0	-5.4
0	13	6	10.0	8.7
0	14	6	19.0	18.5
0	15	6	16.0	-15.5
0	16	6	16.1	-14.7
0	17	6	7.5	9.1
0	18	6	6.1	8.7
0	2	7	26.5	-29.3
0	3	7	12.8	-11.8
0	4	7	18.7	19.1
0	5	7	27.5	27.8
0	6	7	20.3	-16.5
0	7	7	33.5	-36.5
0	8	7	42.7	44.2
0	9	7	23.0	22.6
0	10	7	33.7	-37.0
0	11	8	62.2	-65.9
0	12	8	24.7	-23.8
0	3	8	31.8	32.4
0	5	8	14.8	-15.2
0	6	8	16.3	15.3
0	9	8	8.4	9.5
0	13	8	12.8	13.9
0	15	8	14.5	-16.5
0	2	9	12.9	-13.1
0	4	9	19.4	21.6
0	6	9	35.3	-35.6
0	7	9	22.0	-23.4
0	8	9	28.2	34.9
0	10	9	21.3	-18.3
0	12	9	12.8	14.5
0	1	10	37.5	-44.5
0	2	10	9.2	-9.2
0	3	10	16.2	18.7
0	4	10	9.5	12.2
0	11	10	16.7	-16.6
0	2	11	13.8	-18.0
0	4	11	17.1	18.4
0	6	11	25.5	-31.6
0	8	11	25.4	29.0
0	10	11	18.5	-20.2
0	1	12	21.2	-23.6
0	3	12	8.7	8.1
0	5	12	8.7	-9.7
0	8	12	8.3	-11.0
0	10	12	8.1	12.9
0	4	13	17.0	21.5
0	6	13	16.5	-18.4
0	8	13	18.4	20.9
0	10	13	11.8	-13.7
0	0	8	75.0	65.0
0	0	10	12.1	11.9
0	0	14	16.5	-20.9
1	2	0	23.5	-20.7
1	3	0	16.8	16.7
1	4	0	32.6	29.2
1	5	0	26.1	-21.6
1	6	0	7.4	-2.1
1	7	0	6.6	7.4
1	8	0	20.7	14.6
1	9	0	11.7	19.3
1	10	0	21.9	-15.6
1	13	0	28.4	30.9
1	15	0	23.9	-22.7
1	17	0	21.2	20.4
1	19	0	11.0	-10.9
1	2	1	5.9	4.9
1	5	1	9.7	-5.5
1	7	1	8.3	8.7
1	9	1	18.2	-13.2
1	10	1	49.5	-48.1
1	11	1	15.8	15.7
1	12	1	14.4	13.1
1	18	1	10.8	10.7
1	0	2	58.0	-53.7
1	2	2	44.6	-44.7
1	6	2	9.1	-8.4
1	7	2	13.1	10.9
1	8	2	21.8	-19.9
1	9	2	19.5	15.9
1	10	2	8.7	-6.6
1	11	2	26.6	-26.8
1	13	2	27.4	27.8
1	15	2	25.7	-26.7
1	17	2	17.6	16.6
1	18	2	7.4	-6.5
1	1	3	10.4	-10.1
1	2	3	25.4	25.3
1	4	3	9.4	5.7
1	5	3	7.8	-7.8
1	6	3	94.4	-95.6
1	7	3	50.3	52.7
1	8	3	76.9	76.7
1	9	3	40.8	-39.6
1	10	3	36.4	-37.8
1	11	3	19.5	16.2
1	12	3	22.5	21.5
1	18	3	8.7	6.8
1	1	4	46.6	-47.3
1	2	4	40.3	39.4
1	3	4	23.2	23.7
1	4	4	30.2	25.1
1	5	4	9.1	-9.6
1	6	4	35.4	36.7
1	7	4	22.3	-20.2
1	8	4	33.6	-29.8
1	9	4	18.1	15.1
1	10	4	13.1	-11.3
1	11	4	8.4	-6.8
1	12	4	20.5	19.0
1	15	4	23.0	-22.7
1	16	4	8.9	8.3
1	17	4	13.7	13.8
1	1	5	15.5	-14.9
1	2	5	38.1	-35.0
1	3	5	8.3	-6.2
1	4	5	48.4	51.6
1	5	5	28.2	-30.0
1	6	5	42.4	-40.8
1	7	5	47.7	43.4
1	8	5	50.2	47.5
1	9	5	34.7	-35.8
1	10	5	22.8	-21.8
1	12	5	12.3	11.0
1	18	5	7.4	9.9
1	0	6	37.7	-36.1
1	1	6	29.2	-32.8
1	2	6	49.8	48.0
1	3	6	30.5	30.2
1	4	6	31.5	-27.7
1	5	6	15.0	-15.6
1	6	6	17.2	15.5
1	7	6	20.9	-20.0
1	8	6	13.7	11.5
1	9	6	13.4	12.8
1	11	6	17.3	16.9
1	12	6	12.3	11.9
1	14	6	13.5	-12.8
1	15	6	10.9	-12.3
1	16	6	13.9	13.5
1	17	6	9.6	11.5
1	18	6	5.1	-6.3
1	1	7	16.2	-17.6
1	3	7	33.2	32.7
1	4	7	18.7	18.3
1	5	7	24.7	-27.7
1	6	7	30.5	-31.4
1	7	7	19.0	17.4
1	8	7	21.9	19.9
1	9	7	26.9	-24.8
1	10	7	17.3	-18.7
1	11	7	12.4	10.7
1	12	7	8.6	10.1
1	13	7	12.7	-12.1
1	0	8	49.4	-54.0
1	1	8	17.6	-18.4
1	2	8	41.9	39.7
1	3	8	16.4	17.4
1	5	8	21.5	-20.9
1	6	8	20.4	19.4
1	7	8	17.5	-14.5
1	8	8	9.7	9.5
1	10	8	14.8	-15.1
1	15	8	6.6	-7.3
1	16	8	18.5	19.9
1	0	9	8.0	-7.3
1	1	9	11.4	10.7
1	3	9	14.1	14.5
1	4	9	12.6	-10.8
1	5	9	14.5	-12.7
1	6	9	15.6	-16.0
1	7	9	26.9	28.2
1	8	9	23.1	21.7
1	9	9	23.1	-20.4
1	10	9	8.6	-8.5
1	13	9	8.6	-9.0
1	0	10	27.9	-32.9
1	2	10	28.1	27.6
1	4	10	20.5	-22.0
1	10	10	14.4	-13.5
1	12	10	10.5	10.4
1	2	11	13.3	12.3
1	5	11	12.3	-12.8
1	7	11	28.4	29.5
1	11	11	11.8	11.7
1	0	12	28.8	-31.1
1	2	12	17.3	18.3
1	12	12	7.7	9.1
1	5	13	15.7	-16.1
1	7	13	14.6	16.2
1	9	13	12.8	-13.9
1	0	14	13.8	-15.1
1	1	14	8.7	6.8
1	2	14	14.9	15.8
1	4	14	8.3	-8.7
1	-9	1	31.2	34.9
1	-4	2	75.5	-82.7
1	-6	2	98.6	-95.3
1	-8	2	47.7	-32.3
1	-9	2	10.0	9.4
1-10		2	25.3	-22.7
1-11		2	16.3	13.0
1-12		2	14.0	-10.1
1-13		2	12.4	9.7
1-14		2	12.1	9.1
1-15		2	13.1	13.5
2	-5	2	16.9	11.5
2	-6	2	60.1	-55.5
2	-7	2	27.6	-27.2
2	-8	2	61.2	-61.3
2	-9	2	17.0	-16.2
2-10		2	36.2	-36.6
2-12		2	20.5	-15.5
2-14		2	12.1	-12.1
2-16		2	11.5	-11.3
3	-2	2	82.9	92.7
3	-4	2	42.2	47.8
3	-5	2	28.0	-28.1
3	-6	2	7.8	-0.8
3	-7	2	10.0	7.6
3	-8	2	10.9	9.1
3	-9	2	24.1	-23.1
3-10		2	15.6	14.4
3-11		2	27.5	-25.3
3-13		2	28.9	-29.1
3-15		2	15.7	-17.1
4	-3	2	21.0	15.8
4	-5	2	29.7	28.4
4	-	2	32.5	24.3
4	-7	2	25.1	23.6
4	-8	2	32.3	33.2
4-10		2	26.4	22.7
4-12		2	20.7	18.4
4-15		2	7.7	-6.6
5	-1	2	7.6	-5.1
5	-2	2	37.2	-35.5
5	-3	2	23.2	23.1
5	-7	2	29.5	-30.2
5	-5	2	11.4	12.5
5	-6	2	8.7	-8.5
5	-7	2	37.1	38.1
5	-9	2	25.4	26.5
5-10		2	13.3	-12.4
5-11		2	26.2	23.1
5-13		2	24.0	21.5
5-15		2	17.4	14.7
6	-2	2	24.6	-19.5
6	-3	2	42.6	-37.7
6	-4	2	22.6	19.4
6	-5	2	57.6	-58.6
6	-6	2	16.7	-15.4
6	-7	2	27.5	-25.2
6	-8	2	25.6	-20.5
6	-9	2	11.2	-7.4
6-10		2	19.6	-20.1
6-11		2	17.2	16.4
6-13		2	14.2	-12.2
6-17		2	12.2	-17.1
7	-1	2	18.9	17.1
7	-3	2	19.7	-19.5
7	-4	2	10.1	-5.5
7	-5	2	42.0	-41.1
7	-6	2	6.9	5.8
7	-7	2	27.9	-26.4
7	-8	2	15.5	15.9
7	-9	2	32.3	-32.4
7-10		2	12.0	9.9
7-11		2	34.4	-29.2
7-13		2	23.3	-22.5
7	-15	2	13.8	-13.9
8	-1	2	41.6	41.3
8	-4	2	17.2	-15.8
8	-5	2	54.7	57.2
8	-6	2	28.9	-24.1
8	-7	2	36.0	34.3
8	-8	2	11.4	-8.5
8-10		2	14.1	15.1
8-13		2	11.6	-8.6
9	-2	2	27.0	29.3
9	-4	2	11.7	12.5
9	-5	2	26.4	26.2
9	-7	2	37.7	39.3
9	-9	2	17.2	14.8
9-10		2	10.1	9.5
9-11		2	24.0	22.6
9-13		2	21.7	23.5
10	-1	2	41.7	-39.9
10	-2	2	12.0	11.3
10	-3	2	35.0	-34.3
10	-4	2	21.1	20.6
10	-5	2	36.8	-34.3
10	-6	2	19.3	15.1
10	-7	2	11.8	-12.4
10-10		2	24.1	23.3
10-12		2	11.5	11.0
10-13		2	10.5	9.2
11	-2	2	16.7	-14.7
11	-3	2	13.0	-12.8
11	-4	2	16.1	-12.9
11	-5	2	22.8	-23.2
11	-6	2	16.9	-14.6
11	-8	2	26.9	-25.6
11	-9	2	14.2	-12.4
11-11		2	22.8	-19.7
11-13		2	11.2	-12.5
12	-1	2	16.5	16.5
12	-3	2	19.8	16.4
12	-5	2	22.1	22.7
12	-6	2	10.0	-10.2
12	-7	2	10.1	8.8
12	-8	2	24.1	-25.3
12-10		2	16.5	-17.8
13	-1	2	8.6	-3.2
13	-2	2	17.2	15.4
13	-4	2	17.3	13.0
13	-6	2	29.0	26.3
13	-7	2	8.7	9.7
13	-8	2	17.1	14.7
13	-9	2	10.5	10.5
13-10		2	9.0	8.7
14	-1	2	8.7	-9.6
14	-4	2	12.3	14.2
14	-6	2	20.5	19.7
14	-8	2	19.4	20.5
14	-9	2	8.9	-9.0
14	-12	2	9.9	-9.1
14-10		2	14.3	16.4
15	-2	2	23.9	-25.3
15	-4	2	28.3	-29.8
15	-6	2	16.4	-14.7
15	-8	2	10.7	-9.0
15-12		2	7.9	-2.6
16	-1	2	6.3	-9.1
16	-4	2	10.2	-17.3
16	-6	2	21.0	-22.5
16	-8	2	16.0	-16.5
17	-1	2	7.7	-8.0
17	-2	2	21.1	21.4
17	-4	2	14.7	13.7
17	-6	2	6.7	9.5
17	-7	2	8.8	-5.8
18	-1	2	7.8	7.1
18	-2	2	9.5	10.6
18	-3	2	7.6	8.7
18	-4	2	9.0	9.9
18	-5	2	8.9	8.5
18	-6	2	9.1	9.4
C	-4	2	9.3	2.3
0	-6	2	55.9	57.4
0	-8	2	69.2	67.3
0-10		2	50.9	52.1
0-12		2	28.4	26.3
0-14		2	17.2	17.1
2	-1	2	22.2	-20.7
2	-1	2	16.9	21.1
2	-1	2	40.8	-42.7
2	-1	2	8.1	7.7
2	-1	2	60.3	61.6
2	-1	2	11.3	11.6
2	-1	2	50.8	-52.7
2	-1	2	11.4	-8.2
2	-1	2	28.7	31.0
2	-1	2	12.7	-11.9
2	-1	2	10.7	9.8
2	-1	2	60.9	-59.9
2	1	0	7.9	7.6
2	3	0	23.3	29.8
2	3	0	19.3	-13.3
2	4	0	44.8	-42.4
2	5	0	20.9	20.3
2	6	0	26.9	28.1
2	9	0	10.7	-10.6
2	10	0	22.9	-24.4
2	12	0	25.3	27.5
2	14	0	30.8	-32.1
2	1	1	9.1	-7.9
2	2	1	17.6	19.1
2	3	1	36.6	39.3
2	4	1	7.8	-4.5
2	5	1	31.7	-34.9
2	6	1	13.7	-13.6
2	7	1	53.2	59.2
2	8	1	14.4	-14.0
2	9	1	43.8	-46.4
2	10	1	13.5	11.4
2	11	1	24.6	23.6
2	13	1	15.0	-16.0
2	17	1	7.3	6.8
2	1	2	12.8	12.6
2	2	2	55.4	57.3
2	3	2	21.9	-18.5
2	4	2	13.2	-9.0
2	5	2	48.0	49.8
2	6	2	15.4	15.2
2	7	2	19.3	-18.1
2	10	2	28.0	-29.2
2	12	2	21.7	22.2
2	13	2	9.2	-10.1
2	14	2	12.8	-16.1
2	16	2	19.0	18.8
2	1	3	25.3	-23.9
2	2	3	11.0	14.6
2	3	3	8.2	-3.7
2	4	3	14.5	-14.1
2	5	3	51.8	-54.4
2	6	3	24.6	22.7
2	7	3	49.9	51.7
2	8	3	18.6	-15.5
2	9	3	27.4	-29.8
2	11	3	12.7	11.1
2	13	3	13.0	-13.4
2	0	4	57.2	-64.4
2	1	4	41.0	42.8
2	2	4	58.9	63.8
2	3	4	30.2	-31.5
2	4	4	15.9	-11.3
2	5	4	11.4	12.5
2	7	4	21.5	-19.6
2	8	4	19.5	15.7
2	10	4	14.5	6.5
2	11	4	9.1	15.1
2	12	4	10.6	5.0
2	13	4	10.5	-6.1
2	14	4	20.8	-12.4
2	15	4	9.4	7.8
2	1	5	9.5	7.6
2	2	5	18.9	18.1
2	3	5	16.7	12.5
2	4	5	17.3	-16.2
2	5	5	25.0	-26.7
2	6	5	31.5	30.1
2	7	5	32.8	32.9
2	8	5	23.7	-25.0
2	9	5	29.3	-25.5
2	0	6	41.6	-46.6
2	1	6	50.1	50.3
2	2	6	17.8	17.0
2	3	6	18.2	-18.8
2	4	6	18.7	-21.2
2	5	6	11.4	10.2
2	7	6	10.0	8.0
2	9	6	10.5	-8.5
2	11	6	10.6	10.0
2	13	6	9.9	-11.7
2	14	6	11.3	-13.6
2	15	6	17.1	18.4
2	17	6	5.3	-10.2
2	4	7	20.0	-22.4
2	6	7	24.3	24.0
2	7	7	21.3	22.0
2	8	7	21.7	-18.6
2	9	7	15.0	-16.8
2	10	7	10.6	10.2
2	11	7	14.7	15.4
2	12	7	10.0	-10.8
2	16	7	8.5	1.3
2	1	8	22.8	27.2
2	2	8	12.2	13.0
2	3	8	20.8	-23.6
2	4	8	14.5	-15.0
2	5	8	17.9	16.8
2	8	8	12.9	-11.8
2	11	8	12.2	10.3
2	13	8	17.8	-18.1
2	14	8	9.4	-8.7
2	15	8	16.6	17.2
2	1	9	9.1	-5.0
2	2	9	18.4	17.5
2	3	9	25.3	-23.9
2	5	9	21.5	-22.2
2	6	9	18.4	-7.8
2	7	9	6.8	6.8
2	9	9	13.9	15.3
2	10	9	6.6	-7.2
2	12	9	8.6	-7.2
2	0	10	15.0	-19.4
2	1	10	18.4	19.9
2	2	10	10.6	8.9
2	4	10	21.9	-25.1
2	5	10	12.9	15.0
2	7	10	8.9	-2.6
2	9	10	8.3	-7.5
2	11	10	10.2	10.2
2	1	11	17.1	18.8
2	3	11	15.8	16.2
2	10	11	11.2	10.1
2	2	12	26.3	22.4
2	4	12	11.9	-11.0
2	4	13	10.2	-11.4
2	6	13	10.7	12.8
2	8	13	13.0	-13.6
2	1	14	12.0	-16.7
2	1	-5	25.2	-23.1
2	1	-6	20.8	-21.5
2	1	-7	19.6	-19.5
2	1	-8	49.8	-48.5
2	1	-9	17.3	-16.1
2	1	-15	13.8	-13.9
3	1	1	53.2	59.2
3	2	1	14.4	-14.0
3	3	1	43.8	-46.4
3	4	1	13.5	11.4
3	5	1	24.6	23.6
3	6	1	15.0	-16.0
3	7	1	7.3	6.8
3	1	2	12.8	12.6
3	2	2	55.4	57.3
3	3	2	21.9	-18.5
3	4	2	13.2	-9.0
3	5	2	48.0	49.8
3	6	2	15.4	15.2
3	7	2	19.3	-18.1
3	10	2	28.0	-29.2
3	12	2	21.7	22.2
3	13	2	9.2	-10.1
3	14	2	12.8	-16.1
3	16	2	19.0	18.8
3	1	3	25.3	-23.9
3	2	3	11.0	14.6
3	3	3	8.2	-3.7
3	4	3	14.5	-14.1
3	5	3	51.8	-54.4
3	6	3	24.6	22.7
3	7	3	49.9	51.7
3	8	3	18.6	-15.5
3	9	3	27.4	-29.8
3	11	3	12.7	11.1
3	13	3	13.0	-13.4
3	0	4	57.2	-64.4
3	1	4	41.0	42.8
3	2	4	58.9	63.8
3	3	4	30.2	-31.5
3	4	4	15.9	-11.3
3	5	4	11.4	12.5
3	7	4	21.5	-19.6
3	8	4	19.5	15.7
3	10	4	14.5	6.5
3	11	4	9.1	15.1
3	12	4	10.6	5.0
3	13	4	10.5	-6.1
3	14	4	20.8	-12.4
3	15	4	9.4	7.8
3	1

Table 2.3 (cont'd)

H	K	L	F OBS	F CALC
2	1	-10	53.6	-49.2
2	1	-12	23.1	+22.4
2	1	-14	12.9	-11.2
2	2	-3	13.1	-12.8
2	2	-4	45.7	53.3
2	2	-5	15.6	-14.9
2	2	-6	21.5	22.2
2	2	-8	15.9	15.5
2	2	-9	29.4	-29.6
2	2	-11	17.1	-17.5
2	2	-13	16.4	-16.0
2	2	-15	17.3	-16.9
2	3	-2	3.7	3.2
2	3	-3	31.8	34.3
2	3	-4	35.7	39.4
2	3	-5	23.8	24.0
2	3	-6	31.9	37.5
2	3	-7	42.4	45.6
2	3	-8	34.9	37.9
2	3	-9	12.3	11.1
2	3	-10	45.9	44.4
2	3	-12	30.4	24.5
2	3	-14	14.1	16.0
2	4	-2	42.6	-46.0
2	4	-3	21.9	20.2
2	4	-4	4.0	-54.3
2	4	-5	5.5	7.4
2	4	-6	6.0	-5.4
2	4	-7	47.4	46.0
2	4	-9	32.6	29.7
2	4	-11	24.6	21.9
2	4	-12	12.9	-11.2
2	4	-13	26.0	22.9
2	4	-14	12.7	11.1
2	4	-15	20.0	19.9
2	5	-2	19.5	+21.4
2	5	-3	35.5	-42.2
2	5	-4	7.8	-7.9
2	5	-6	30.4	+28.9
2	5	-7	39.0	+40.2
2	5	-8	35.1	-36.4
2	5	-10	20.2	-19.2
2	5	-11	12.6	11.0
2	5	-12	30.3	-32.2
2	5	-14	17.7	-17.6
2	6	-2	26.5	+25.9
2	6	-4	17.2	19.0
2	6	-5	36.2	-37.7
2	6	-6	46.2	41.1
2	6	-7	34.1	-38.2
2	6	-9	33.0	-29.9
2	6	-10	12.3	10.3
2	6	-11	25.5	-27.3
2	6	-13	21.6	-17.7
2	6	-15	15.9	+15.4
2	7	-2	17.2	17.5
2	7	-4	16.8	-13.9
2	7	-5	39.1	45.7
2	7	-7	36.0	33.6
2	7	-9	20.3	19.0
2	7	-10	12.6	13.2
2	7	-12	13.0	11.5
2	8	-2	13.8	10.5
2	8	-3	19.8	19.0
2	8	-5	35.3	36.5
2	8	-7	19.5	16.9
2	8	-9	17.6	16.5
2	8	-11	21.9	19.2
2	8	-13	24.7	25.5
2	9	-3	35.7	+34.4
2	9	-5	31.7	+33.6
2	9	-6	27.2	24.4
2	9	-7	22.2	+19.9
2	9	-8	17.6	15.4
2	9	-9	19.1	17.4
2	9	-11	11.6	+6.4
2	9	-13	17.2	+15.7
2	10	-2	22.7	+25.6
2	10	-3	22.9	+21.4
2	10	-5	11.8	+9.2
2	10	-7	8.8	+7.0
2	10	-10	13.0	-12.7
2	10	-11	17.3	+14.7
2	11	-3	24.2	26.0
2	11	-5	12.4	10.0
2	11	-6	17.9	-15.7
2	11	-7	12.9	11.3
2	11	-8	30.4	+25.0
2	11	-9	15.0	16.7
2	12	-2	13.4	+14.0
2	12	-4	9.0	8.4
2	12	-5	13.9	11.5
2	12	-6	16.3	13.4
2	12	-7	17.0	17.2
2	12	-8	9.2	10.5
2	12	-9	14.7	14.1
2	12	-12	12.7	3.4
2	13	-3	15.0	-11.7
2	13	-5	16.4	+20.6
2	13	-6	21.8	21.2
2	13	-7	16.2	-16.2
2	13	-8	25.3	24.0
2	13	-10	16.5	17.3
2	14	-2	25.9	+27.3
2	14	-3	9.2	8.6
2	14	-4	21.7	+22.0
2	14	-6	12.7	+8.5
2	14	-7	17.6	+16.5
2	14	-8	12.0	-11.1
2	14	-9	11.5	+10.5
2	14	-10	8.7	+9.4
2	15	-4	17.6	-16.4

H	K	L	F OBS	F CALC
2	15	-6	24.1	+21.7
2	15	-8	15.7	-14.8
2	15	-10	15.5	+16.0
2	16	-3	22.7	+25.4
2	16	-4	11.5	15.6
2	17	-3	14.6	11.9
2	17	-4	13.4	10.1
2	17	-5	11.7	12.6
2	1	-6	44.8	+36.7
2	0	-8	20.2	+24.7
2	0	-11	15.7	+15.1
3	4	-2	4.7	7.7
3	5	-2	27.7	31.7
3	0	-2	20.5	+26.6
3	1	-2	12.5	15.1
3	10	-2	12.5	10.1
3	11	-2	21.9	22.7
3	12	-2	21.0	+21.9
3	15	-2	7.6	2.6.4
3	1	-1	15.9	+17.0
3	2	-1	3.4	3.9
3	3	-1	11.8	11.4
3	4	-1	27.2	+27.0
3	6	-1	27.5	27.9
3	8	-1	31.9	+35.9
3	9	-1	20.0	+23.9
3	10	-1	3.3	3.0
3	12	-1	9.4	-9.2
3	14	-1	9.1	9.9
3	0	-1	4.8	6.4
3	1	0	16.9	-16.5
3	3	0	30.2	+40.1
3	4	0	26.9	30.1
3	5	0	2.3	3.0
3	6	0	22.7	-22.0
3	7	0	1.6	1.6
3	8	0	26.5	+28.1
3	9	0	22.4	22.4
3	1	1	19.2	20.9
3	2	1	2.0	+29.7
3	4	1	25.0	22.0
3	5	1	7.8	-8.4
3	6	1	30.3	+30.1
3	9	1	14.3	11.7
3	10	1	20.4	17.8
3	12	1	13.3	+11.2
3	1	2	41.2	42.3
3	2	2	10.3	-9.7
3	3	2	38.7	+38.2
3	4	2	10.5	14.5
3	5	2	20.7	22.9
3	6	2	10.9	-9.5
3	7	2	10.3	+15.3
3	8	2	8.6	+5.3
3	9	2	10.4	+8.7
3	11	2	26.6	25.6
3	13	2	18.3	+17.2
3	15	2	17.9	17.3
3	1	3	13.6	13.1
3	2	3	28.4	27.6
3	3	3	20.3	+21.0
3	4	3	15.0	+11.5
3	5	3	22.1	21.0
3	6	3	23.1	24.4
3	7	3	24.2	+23.8
3	8	3	23.5	+21.8
3	9	3	15.0	12.6
3	10	3	13.3	12.2
3	11	3	10.9	+6.6
3	2	4	21.6	+20.2
3	3	4	23.9	+23.4
3	5	4	13.6	15.8
3	7	4	12.6	+11.6
3	11	4	15.3	12.1
3	13	4	15.8	+15.1
3	1	5	19.4	17.4
3	3	5	18.8	+14.9
3	4	5	17.2	+15.7
3	5	5	26.9	27.2
3	6	5	18.0	17.2
3	7	5	21.9	+20.7
3	8	5	16.7	+20.0
3	9	5	18.9	16.8
3	10	5	15.2	14.7
3	11	5	10.6	+8.4
3	13	5	11.6	12.0
3	0	6	18.8	23.2
3	1	6	20.8	21.1
3	2	6	13.4	+11.4
3	4	6	15.2	+14.2
3	12	6	15.9	+14.7
3	3	7	13.1	+12.0
3	5	7	16.8	17.3
3	6	7	10.9	10.3
3	7	7	22.4	+21.4
3	8	7	15.2	+15.8
3	9	7	16.2	16.4
3	12	7	12.4	11.3
3	11	7	11.7	+10.5
3	0	8	22.4	20.9
3	1	8	18.8	9.8
3	2	8	9.4	+14.7
3	3	8	15.4	+6.3
3	9	8	13.1	+12.3
3	5	9	12.9	12.1
3	7	9	17.3	+19.2
3	0	10	18.0	18.8
3	2	10	17.6	+16.2
3	4	10	12.3	10.0
3	1	-3	13.9	+13.5
3	1	-4	18.6	22.8
3	1	-5	23.3	+25.0
3	1	-6	39.0	39.1
3	1	-7	8.8	5.2
3	1	-8	25.4	29.3

H	K	L	F OBS	F CALC
3	1	-9	18.2	-18.3
3	1	-11	23.3	-23.8
3	2	-3	25.3	28.2
3	2	-4	8.9	8.4
3	2	-5	10.1	11.3
3	2	-6	17.5	19.4
3	2	-7	9.1	7.3
3	2	-9	20.0	20.0
3	2	-9	37.6	35.9
3	2	-10	42.9	40.8
3	2	-12	18.5	16.6
3	2	-14	15.2	14.0
3	3	-3	39.2	45.4
3	3	-5	36.8	39.7
3	3	-6	17.1	+18.2
3	3	-7	18.9	19.1
3	3	-8	24.9	+24.9
3	3	-9	25.0	24.8
3	3	-11	44.0	41.3
3	3	-13	25.0	25.2
3	3	-15	8.7	8.1
3	4	-3	38.0	+43.7
3	4	-4	27.4	+26.7
3	4	-5	34.9	+36.1
3	4	-6	31.7	+33.2
3	4	-7	28.6	+27.8
3	4	-8	20.0	+18.5
3	4	-10	22.9	+20.4
3	4	-12	32.0	+31.0
3	4	-13	13.3	9.4
3	4	-14	21.8	+21.9
3	5	-3	10.4	-9.2
3	5	-4	43.8	44.6
3	5	-5	31.9	+31.7
3	5	-6	36.5	29.1
3	5	-7	43.1	+40.4
3	5	-8	34.3	+33.1
3	5	-10	14.5	12.2
3	5	-11	31.5	+30.8
3	5	-12	22.3	+21.0
3	5	-15	19.9	-19.0
3	6	-3	55.2	56.6
3	6	-5	49.8	48.8
3	6	-6	30.2	29.1
3	6	-7	31.9	32.5
3	6	-8	19.7	18.1
3	6	-9	14.2	14.4
3	6	-12	21.1	19.9
3	6	-14	16.1	15.5
3	7	-2	14.5	15.2
3	7	-13	21.7	22.8
3	7	-4	19.5	+18.1
3	7	-5	25.9	24.5
3	7	-6	11.1	-11.9
3	7	-7	28.1	27.4
3	7	-9	30.6	29.6
3	7	-11	21.1	18.5
3	7	-13	21.7	22.8
3	8	-3	26.7	+26.4
3	8	-4	12.9	-11.6
3	8	-5	33.1	+35.7
3	8	-7	30.4	+28.3
3	8	-9	9.2	-8.4
3	9	-3	16.7	+15.3
3	9	-4	16.9	+14.5
3	9	-7	21.4	+23.3
3	9	-9	18.7	+18.9
3	9	-10	13.3	+12.8
3	9	-11	15.2	+14.9
3	10	-3	12.5	9.8
3	10	-4	14.5	+15.4
3	10	-5	12.7	14.2
3	10	-6	14.9	+15.1
3	10	-7	13.1	11.3
3	10	-8	18.8	+19.6
3	10	-10	13.2	+14.9
3	10	-12	12.3	+15.0
3	11	-3	13.0	13.7
3	11	-4	22.0	22.2
3	11	-5	15.2	15.1
3	11	-6	13.2	10.3
3	11	-7	15.4	12.9
3	11	-9	13.2	14.3
3	11	-11	14.3	12.4
3	12	-3	26.6	-26.4
3	12	-4	10.9	-1.4
3	12	-6	22.4	22.4
3	12	-7	15.3	+12.8
3	12	-8	31.7	27.6
3	12	-10	17.4	16.2
3	13	-4	22.3	+23.2
3	14	-5	10.4	11.7
3	13	-6	15.1	+16.0
3	13	-7	18.3	+17.6
3	13	-9	14.0	+13.6
3	14	-3	12.9	10.3
3	14	-5	12.7	11.7
3	14	-6	14.5	+16.7
3	14	-8	16.7	+18.1
3	15	-4	17.1	19.3
3	15	-6	13.4	13.0
3	0	-4	22.4	+20.4
3	0	-8	10.9	8.4
3	0	-8	43.3	+40.3
3	0	-10	23.3	+24.8
3	0	-12	24.4	+24.1
3	0	-14	10.8	-9.1
4	1	-3	22.4	15.9
4	2	-3	35.8	31.6
4	3	-3	41.4	+34.0
4	4	-3	24.6	+20.0
4	5	-3	39.8	37.8
4	7	-3	36.6	+36.4
4	11	-3	14.3	+13.4

H	K	L	F OBS	F CALC
4	13	-3	15.7	15.2
4	0	-2	40.5	42.4
4	1	-2	16.5	+12.9
4	2	-2	29.7	+31.4
4	4	-2	31.5	34.0
4	5	-2	17.9	17.7
4	6	-2	13.4	+12.0
4	10	-2	20.0	21.7
4	11	-2	10.1	8.5
4	12	-2	20.0	+20.3
4	13	-2	9.6	+7.9
4	1	-1	16.0	15.7
4	2	-1	0.1	2.9
4	3	-1	31.9	+29.6
4	5	-1	20.7	21.3
4	6	-1	11.9	+12.0
4	7	-1	17.9	+18.0
4	9	-1	19.6	20.0
4	10	-1	10.0	8.6
4	11	-1	17.5	+16.6
4	13	-1	9.5	10.5
4	0	0	65.1	41.6
4	1	0	0.5	+6.4
4	2	0	27.6	+32.7
4	4	0	26.3	27.7
4	10	0	20.2	17.2
4	11	0	10.1	8.5
4	12	0	19.7	+20.5
4	14	0	14.1	13.8
4	1	1	17.5	18.5
4	3	1	20.9	+21.5
4	4	1	14.3	14.5
4	5	1	17.4	16.2
4	6	1	10.5	+11.2
4	7	1	10.5	+10.6
4	8	1	9.8	8.0
4	9	1	20.6	20.1
4	10	1	14.3	+12.9
4	11	1	11.5	+13.2
4	0	2	24.7	24.4
4	2	2	28.4	+28.9
4	3	2	21.0	23.4
4	4	2	13.4	+13.6
4	10	2	14.2	11.9
4	12	2	15.4	+15.6
4	14	2	11.1	10.4
4	1	3	14.5	10.6
4	2	3	17.9	+16.3
4	3	3	12.9	+10.7
4	5	3	16.6	17.3
4	7	3	23.8	+24.3
4	8	3	24.0	24.5
4	9	3	17.5	17.2
4	10	3	19.8	+16.5
4	12	3	9.0	8.2
4	0	4	18.8	19.4
4	1	4	9.5	-8.2
4	2	4	9.5	+10.4
4	3	4	9.6	9.7
4	4	4	11.6	-8.7
4	10	4	13.6	11.1
4	12	4	12.0	+10.7
4	2	5	11.5	+11.2
4	3	5	14.1	+17.9
4	4	5	11.6	11.4
4	6	5	20.2	20.1
4	8	5	20.2	+16.5
4	7	5	16.4	+15.6
4	8	5	19.8	14.7
4	9	5	11.1	10.6
4	10	5	10.6	+11.7
4	0	6	10.1	9.6
4	1	6	10.5	+9.5
4	5	6	10.0	+9.8
4	7	6	9.7	6.7
4	3	7	10.0	-9.6
4	4	7	13.9	13.6
4	5	7	9.7	8.0
4	6	7	9.5	-9.5
4	7	7	10.6	-10.4
4	8	7	12.4	11.7
4	1	8	19.3	+18.5
4	3	8	13.4	11.6
4	6	8	10.5	+8.7
4	1	-4	12.9	10.2
4	2	-4	33.0	38.6
4	4	-4	12.2	12.8
4	1	-7	12.2	12.8
4	1	-8	28.6	26.3
4	1	-9	20.4	21.6
4	1	-10	16.0	13.6
4	1	-11	13.7	-9.8
4	1	-12	23.9	25.4
4	2	-4	34.2	+37.0
4	2	-5	17.6	19.3
4	2	-6	22.2	+20.5
4	2	-7	7.3	7.0
4	2	-8	27.3	+26.3
4	2	-9	29.7	30.3
4	2	-10	16.1	+15.5
4	2	-11	40.3	38.1
4	2	-13	11.6	11.2
4	3	-4	18.3	-16.4
4	3	-5	15.2	+15.6
4	3	-6	19.7	+21.0
4	3	-7	21.1	+19.1
4	3	-9	19.7	-20.9
4	3	-9	14.5	+15.9
4	3	-10	24.7	+26.5
4	3	-12	14.3	+14.0
4	3	-13	14.2	11.9
4	3	-14	9.7	+12.0
4	4	-6	9.8	7.6
4	4	-8	29.6	27.4

H	K	L	F OBS	F CALC
4	4	-7	22.7	-24.3
4	4	-8	20.5	21.9
4	4	-9	21.8	-22.6
4	4	-10	15.7	13.0
4	4	-11	28.2	+30.1
4	4	-13	22.3	+24.2
4	4	-15	12.5	+12.2
4	5	-4	10.5	10.8
4	5	-5	26.2	30.1
4	5	-6	11.4	12.2
4	5	-7	12.0	9.4
4	5	-8	25.4	29.0
4	5	-10	16.8	17.1
4	5	-12	14.3	12.8
4	5	-14	10.8	9.7
4	6	-4	9.4	-9.8
4	6	-5	26.3	28.8
4	6	-6	14.9	+18.0
4	6	-7	17.9	17.0
4	6	-8	22.2	+23.6
4	6	-9	16.8	17.1
4	6	-11	14.3	16.4
4	6	-13	23.2	25.6
4	6	-15	16.4	20.3
4	7	-4	14.3	+13.3
4	7	-5	30.3	+33.7
4	7	-6	9.1	-9.2
4	7	-7	15.3	+14.0
4	7	-8	13.7	+12.5
4	7	-10	10.1	-11.8
4	8	-7	23.2	+22.9
4	8	-9	20.1	+16.9
4	8	-11	20.0	+19.2
4	8	-13	18.2	+19.9
4	8	-15	14.3	+17.8
4	9	-5	23.2	26.2
4	9	-7	23.8	23.9
4	9	-10	11.6	+12.1
4	10	-7	10.1	9.8
4	10	-8	11.6	12.9
4	10	-9	20.0	21.4
4	10	-11	22.3	16.6
4	10	-13	11.3	12.9
4	11	-4	14.3	14.2
4	11	-6	14.3	13.6
4	11	-7	11.6	+14.5
4	11	-8	19.8	22.4
4	11	-10	22.3	21.5
4	11	-12	11.5	10.5
4	12	-4	16.3	+19.3
4	12	-6	14.0	+16.9
4	12	-8	11.0	-9.3
4	12	-9	13.0	+12.9
4	12	-11	9.4	+10.3
4	13	-4	9.6	-7.3
4	13	-6	13.3	+15.8
4	13	-8	17.8	+19.3
4	13	-10	12.9	+15.4
4	14	-4	14.7	18.4
4	14	-6	15.1	16.0
4	0	-6	29.2	30.2
4	0	-8	9.0	9.7
4	0	-10	21.8	23.9
4	0	-12	17.4	13.2
4	16	-4	9.6	+11.7
4	16	-6	7.3	-8.8
4	16	-8	8.6	+10.2
5	1	-3	5.8	-2.6
5	2	-3	12.7	+16.0
5	4	-3	16.0	15.5
5	5	-3	13.7	11.7
5	6	-3	30.4	+30.9
5	7	-3	10.9	+8.9
5	8	-3	25.6	24.9
5	10	-3	13.8	+14.1
5	12	-3	10.3	10.8
5	2	-4	10.0	+8.1
5	3	-4	16.9	16.7
5	11	-4	10.9	+8.7
5	12	-4	12.7	+11.2
5	13	-4	9.4	9.3
5	0	-2	11.0	+10.8
5	1	-2	22.7	+24.6
5	2	-2	7.0	9.6
5	3	-2	17.9	17.9
5	4	-2	8.1	7.3
5	6	-2	12.2	+13.8
5	8	-2	12.9	+12.4
5	7	-2	13.4	10.6
5	11	-2	13.2	+12.8
5	12	-2	10.2	-8.4
5	13	-2	13.0	14.1
5	1	-1	7.4	4.9
5	3	-1	13.2	+10.7
5	4	-1	23.0	22.1
5	5	-1	9.0	6.8
5	6	-1	28.5	+25.2
5	7	-1	11.1	9.1
5	8	-1	26.5	21.3
5	10	-1	11.1	+12.9
5	12	-1	8.6	8.7
5	0	0	17.5	+19.5
5	1	0	19.4	+18.7
5	3	0	19.0	19.0

Table 2.4

Bond lengths (Å) and angles (degrees) with standard deviations in parentheses.

Fe - C distances

Fe - C(1)	2.067(10)	Fe - C(6)	2.006(14)
Fe - C(2)	2.014(14)	Fe - C(7)	2.065(13)
Fe - C(3)	2.006(12)	Fe - C(8)	2.040(14)
Fe - C(4)	2.056(14)	Fe - C(9)	2.044(14)
Fe - C(5)	2.055(12)	Fe - C(10)	2.026(16)

Mean value = 2.038 ± 0.007

C - C distances in cyclopentadienyl rings

C(1) - C(2)	1.433(16)	C(6) - C(7)	1.402(20)
C(2) - C(3)	1.380(17)	C(7) - C(8)	1.401(19)
C(3) - C(4)	1.385(20)	C(8) - C(9)	1.352(21)
C(4) - C(5)	1.415(19)	C(9) - C(10)	1.409(24)
C(5) - C(1)	1.457(16)	C(10) - C(6)	1.367(23)

Mean value = 1.400 ± 0.011

Other bond lengths

N - O	1.263(15)	C(11) - C(12)	1.466(19)
N - C(1)	1.393(14)	C(11) - C(13)	1.495(24)
N - C(11)	1.508(15)	C(11) - C(14)	1.564(20)

Table 2.4 (cont'd)

Bond angles in the cyclopentadienyl rings

C(1) – C(2) – C(3)	108.0(1.1)	C(6) – C(7) – C(8)	104.0(1.2)
C(2) – C(3) – C(4)	110.2(1.1)	C(7) – C(8) – C(9)	111.0(1.3)
C(3) – C(4) – C(5)	108.7(1.1)	C(8) – C(9) – C(10)	104.6(1.4)
C(4) – C(5) – C(1)	106.5(1.1)	C(9) – C(10) – C(6)	106.7(1.4)
C(5) – C(1) – C(2)	106.5(1.0)	C(10) – C(6) – C(7)	110.8(1.3)

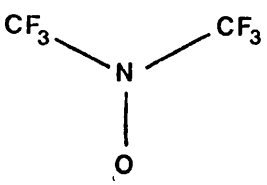
Mean value = 108.0 (1.1)

Other bond angles

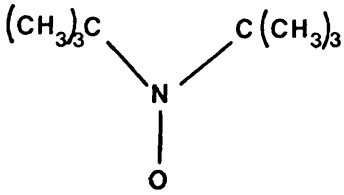
C(1) – N – O	116.1(1.0)	N – C(11) – C(13)	106.4(1.1)
C(11) – N – O	118.5(1.0)	N – C(12) – C(14)	107.4(1.0)
N – C(1) – C(2)	131.5(1.0)	C(12) – C(11) – C(13)	110.2(1.3)
N – C(1) – C(5)	122.0(1.0)	C(12) – C(11) – C(14)	110.1(1.1)
N – C(11) – C(12)	111.7(1.0)	C(13) – C(11) – C(14)	111.1(1.2)
		C(1) – N – C(11)	125.4(0.9)

Table 2.5

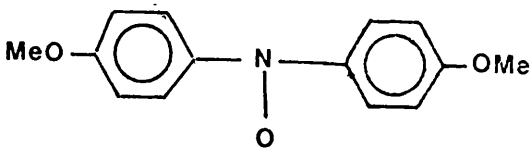
Structure	N-O (Å)	C-N-C (deg.)	(deg.)	Ref.
1	1.26±0.03	120.9±2.0	21.9	9
2	1.28±0.03	126.0±3.0	assumed planar	10
3	1.23±0.05	124.0±5.0	0	11
4	1.291±0.007	125.4±0.5	15.8	12
5	1.277±0.008	114.7±0.7	0	13
6	1.308±0.022	121.0±1.5	24	14
7	1.267±0.008	114.8±0.5	0	15
Bu^+-ferrocenyl nitroxide	1.263±0.015	125.4±0.9	0	
Average	1.278±0.022	123.3±2.4		



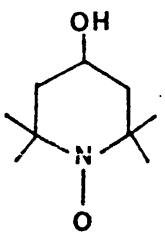
1



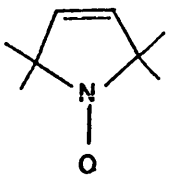
2



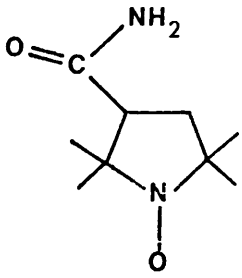
3



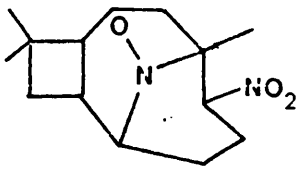
4



5



6



7

Table 2.6

Short contact distances (Å)

(a) Intermolecular contacts less than 3.6 Å.

C(10)····O(2^{I})	3.434	C(17)····O(2^{I})	3.515
C(5)····O(2^{I})	3.511		

(b) Some important intramolecular contacts

O(2)····C(16)	2.596	C(5)····C(15)	3.149
O(2)····C(17)	3.244	Fe····N	3.112
Fe····O	3.629		

Position I is at 1 + x, y, z.

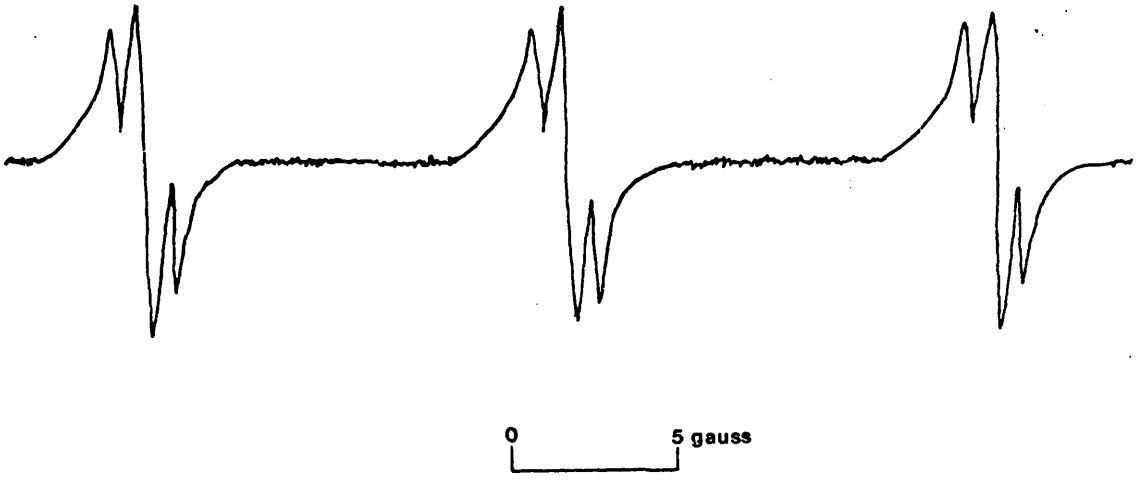


Figure 2.1 : E.s.r. spectrum of t-butylferrocenylnitroxide in CCl_4 solution.

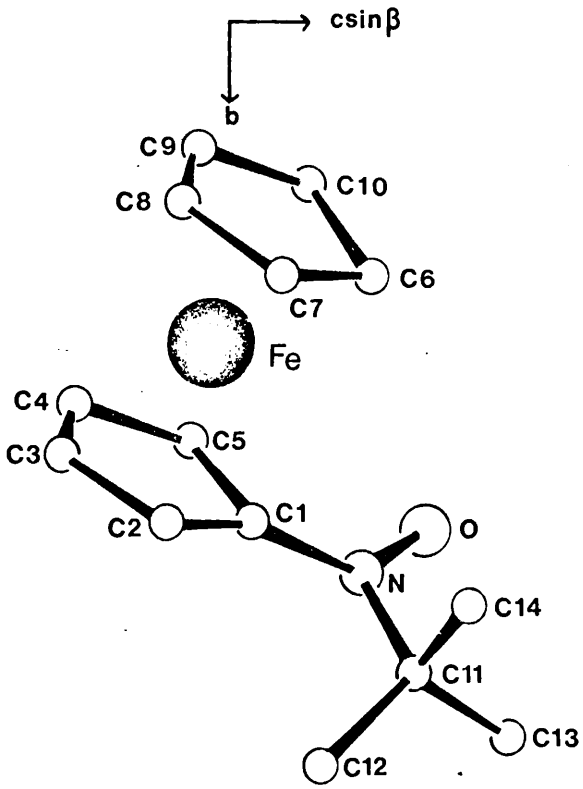


Figure 2.2 : The molecular structure of t-butylferrocenylnitroxide.

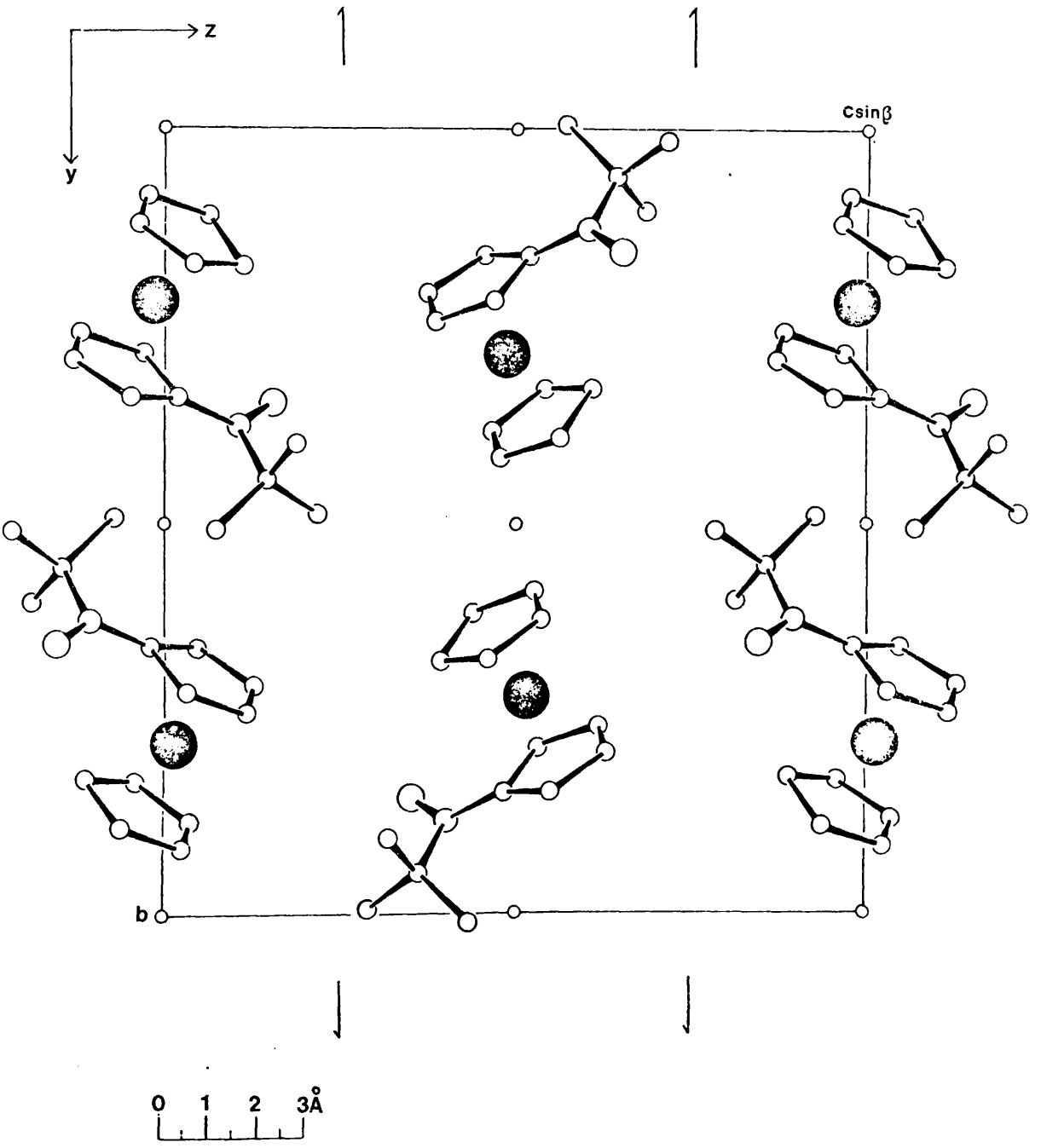
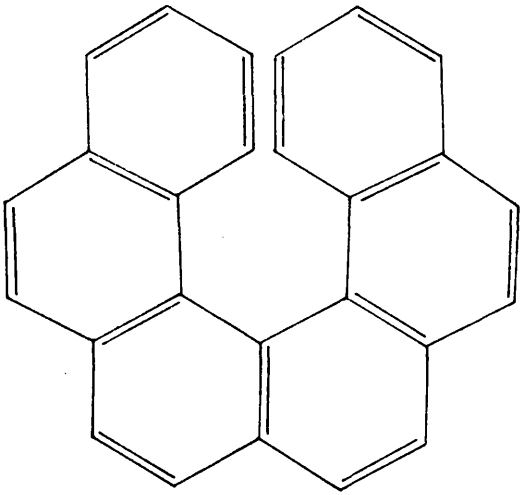


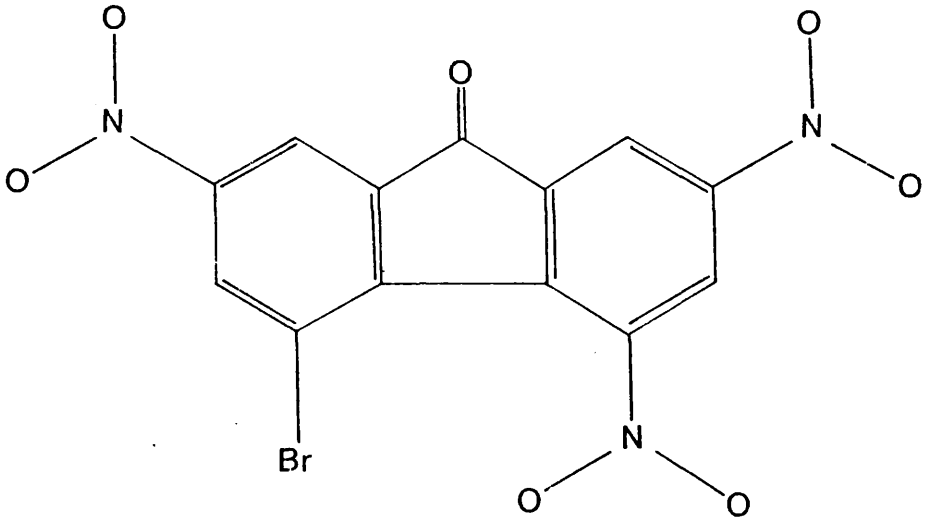
Figure 2.3 : The crystal structure of t-butylferrocenylnitroxide projected along a*.

CHAPTER 3

THE CRYSTAL AND MOLECULAR STRUCTURE OF THE 1:1 COMPLEX OF HEXAHELICENE WITH 4-BROMO-2,5,7-TRINITROFLUORENONE.



(1)



(2)

3.1. Introduction.

Hexahelicene (1) was first synthesised in 1956 by Newman et al[1], and its structure is of great interest because of the severe overcrowding of the terminal rings. To relieve this overcrowding, the molecule must assume a non-planar conformation, and the two aspects of the structure which are of most interest are (i) the extent of the deviation from planarity, and (ii) the effect, if any, which this deviation from planarity has on the bond lengths and angles of the molecule. Preliminary answers to these questions were given when the structure of the 1:1 complex of hexahelicene with 4-bromo-2,5,7-trinitrofluorenone (2) was solved by Robertson et al[2]. The hexahelicene molecule was shown to have the expected helical structure, but because of the large number of atoms in the asymmetric unit (100) and the large number of observed intensities (6,254), only a limited least-squares refinement of the structure was possible using the computing facilities then available at Glasgow. However, the introduction of the XRAY70 system of programs onto the Univac 1108 computer at the National Engineering Laboratory, East Kilbride, enabled the refinement of the structure to be completed. The details of this refinement are described in section 3 of this chapter, and the resulting structural parameters are discussed in section 4.

3.2 Experimental.

Crystal Data.

$2C_{26}H_{16}$, $2C_{13}H_4N_3O_7Br$, $\frac{1}{2}C_6H_6$, M = 1484.0. Triclinic, $\underline{a}$ = 9.30(2), $\underline{b}$ = 20.63(3), $\underline{c}$ = 18.90(3), $\underline{\alpha}$ =114.9(3), $\underline{\beta}$ =93.7(3), $\underline{\gamma}$ =98.7(3). $\underline{U}$ = 3219.0A, $\underline{D}_m$ = 1.52, Z = 2, $\underline{D}_c$ = 1.52. $\mu(CuK_\alpha)$ = 24.1 cm^{-1}. Space group $P\bar{1}$ (No.2).

Data Collection.

The intensity data were collected using a small crystal of dimensions 0.25 x 0.15 x 0.15 mm^3 mounted along $\underline{a}$. Multiple-film equi-inclination Weissenberg photographs were taken of the 0kl - 8kl reciprocal lattice nets using CuK_α radiation, and the intensities of some 6254 reflections were measured. No absorption corrections were applied to the data.

Refinement of the Structure.

The structure was solved by the heavy-atom method,and a random sample of about 2,000 reflections were used in the initial refinement. The hexahelicene and 4-bromo-2,5,7-trinitrofluorenone (B.T.N.F) molecules were refined during alternate cycles of isotropic least-squares refinement, and convergence was reached with R = 19%. The resulting atomic parameters were used as the starting point for the refinement

on the Univac 1108. Two cycles of full-matrix, isotropic least-squares refinement were carried out, using the XRAY70 program ORFLS, after which R was 18%. A difference map calculated at this stage revealed the presence of a diffuse circle of electron density around the origin, indicating that a disordered solvent molecule (benzene) is located at that point in the unit cell. The omission of this solvent molecule explains the relatively large discrepancy between the observed and previously-calculated densities (1.52 and 1.49 respectively); the density calculated with the solvent molecule included is 1.52.

The difference map also showed that one of the two BTNF molecules in the asymmetric unit was disordered about the 2-fold rotation axis of the fluorenone residue (along the line of the carbonyl group), the two orientations being populated approximately in the ratio 2:1. Because of the 2-fold symmetry of the 2,7-dinitrofluorenone residue, the only difference in the two orientations is the interchange of the 4-bromo and 5-nitro groups. The disorder was thus accounted for by introducing two sets of atoms for the 4-bromo and 5-nitro groups, the coordinates of each set of atoms being those determined from the difference map. Each disordered atom was assigned an isotropic temperature factor which had the same value as that of the corresponding atom in the other BTNF molecule, and a further two cycles of least-squares refinement were carried out, during which only the disordered bromine atom positional and population parameters were allowed to vary,

with the population parameters of the disordered nitro group being constrained to be equal to the population parameters of the appropriate bromine atoms. The R-value was reduced to 17%, and the resulting population parameters for the two sets of atoms were 0.69 and 0.31. These values were not refined during the subsequent cycles of least-squares analysis.

The refinement was completed with four cycles of block-diagonal least-squares analysis with anisotropic temperature factors, during which neither of the partially-occupied nitro positions were refined. Hydrogen atoms were included in their calculated positions (Table 3.3), but were not refined, and electron density was included around the origin to allow for the disordered solvent molecule. The final value of R was 10.9%. During the final two cycles of refinement, the data were weighted according to the following scheme:

$$\text{Weight } (W) = X \times Y$$

If $A \times F_{obs} > F_{calc}$, $W = 0.000000001$.

If $\sin\theta > B$, $X = 1$, else $X = \sin\theta/B$.

If $C > F_{obs}$, $Y = 1$, else $Y = C/F_{obs}$.

The final values of A, B, and C were 0.1, 1.0, and 20.0 respectively. The final fractional coordinates and temperature factors are listed in Tables 3.1 and 3.2 respectively, while the observed structure amplitudes and calculated structure factors are listed in Table 3.4. The atomic numbering system is shown in Figure 3.1.

The estimated standard deviations of one of the hexahelicene molecules

are, on average, about twice those of the other hexahelicene molecule in the asymmetric unit; this can be attributed to a slight disorder of the molecule, as a result of the proximity of its ring 5, in particular atoms C(15) and C(16), to the disordered BTNF bromc and nitro groups. The hexahelicene and BTNF molecules which are not disordered are jointly labelled Complex 1, while the disordered hexahelicene and BTNF molecules are labelled Complex 2.

3.3 Description and Discussion of the Structure.

A view of the structure projected along $\underline{a}^*$ is given in Figure 3.2. The unit cell contains four hexahelicene molecules and four BTNF molecules, with a disordered solvent molecule occupying a cavity between adjacent hexahelicene and BTNF molecules at the origin. Two of the hexahelicene molecules are the left-handed enantiomer and two the right-handed enantiomer, each of the former being related to each of the latter by a centre of symmetry. The determination of the absolute configuration of (-)-2-bromohexahelicene by Lightner et al[3] enabled them to show that (-)-hexahelicene has the absolute configuration of a left-handed helix. Each BTNF molecule is sandwiched between two hexahelicene molecules, with rings 2 and 3 of the BTNF molecule lying almost parallel to rings 1 and 2 or 5 and 6 of each of the adjacent hexahelicene molecules, at approximately van der Waals distances. Intermolecular C...C contact distances less than 3.5Å are listed

in Table 3.5. The crystal structure is thus built up of alternate donor (hexahelicene) and acceptor (BTNF) molecules, orientated to allow the maximum overlap of their respective π-molecular orbitals. However, the C...C contacts in Table 3.5 indicate more effective overlaps between the Complex 1 hexahelicene molecule and the two BTNF molecules than between the Complex 2 hexahelicene molecule and the BTNF molecules.

The bond lengths of the hexahelicene and BTNF molecules are listed in Table 3.6 , and their bond angles in Table 3.7. The dimensions of the Complex 1 hexahelicene molecule agree well with those determined for 2-bromohexahelicene[3] and the isomorphous 2-methyl-hexahelicene[4] , and indicate that the helical conformation of the hexahelicene molecule is achieved with little deviation of the bond lengths and angles from their expected values. No meaningful comment can be made about the bond lengths and angles of the disordered hexahelicene molecule because of their high estimated standard deviations. Moreover, comparison of equivalent bond lengths and angles in the two hexahelicene molecules suggests that the standard deviations of the disordered molecule are too optimistic. The following dicussion of the bond lengths and angles in hexahelicene is thus based on the parameters of the Complex 1 molecule only.

Since the hexahelicene molecule has a two-fold axis of symmetry (along the bond C(11) - C(24)), the bond lengths of the two equivalent

halves of the molecule can be averaged, and the resulting values are given in Table 3.8; the average root mean square difference in the bond lengths of the equivalent halves of the molecule is 0.020Å. In addition to the mean observed bond lengths, Table 3.8 lists the lengths of the same bonds as predicted by molecular-orbital and valence-bond calculations. The molecular-orbital bond lengths ($D_{m.o.}$) were calculated from bond-orders (p) which resulted from a π-electron calculation[5] in which a planar hexahelicene molecule was assumed. The relationship[6] $D_{m.o.} = 1.50 - 0.16p$ was used to calculate the bond lengths.

Hexahelicene has 21 different Kekulé structures, and the double-bond character of each bond in the molecule was assessed by averaging these 21 resonance structures. The resulting bond numbers (n) - the double-bond characters + 1 - were used to calculate bond lengths ($D_{v.b.}$) using the relationship derived by Pauling[7]:

$$D_{v.b.} = D_1 - (D_1 - D_2).1.84(n-1)/(0.84n + 0.16)$$

The values used for D_1 and D_2 were 1.504 and 1.334 respectively. The average root mean square differences between the calculated and mean observed bond lengths are 0.019Å and 0.018Å for the $D_{m.o.}$ and $D_{v.b.}$ respectively. None of the differences between the observed and calculated bond lengths listed in Table 3.8 are statistically significant.

It is worth commenting at this point on the observation by

Lightner et al[3,4] that the six bonds bordering the 'inner core' of the helix are all longer than average. They argue that since this is the region of the molecule most subject to distortion, a decrease in the double-bond character of these six bonds is to be expected. However, both the molecular-orbital and valence-bond approximations predict longer than average lengths for the inner core bonds (Table 3.8) from calculations based on a planar molecule.

Inspection of the Complex 1 hexahelicene bond angles shows that only the angles around the inner core deviate significantly from the normal value of 120°, the largest deviation being that of angle C(23) - C(24) - C(25) which has a value of 127°.

The distortion of the molecule is not evenly distributed between the six rings. The deviations of the atoms from the mean planes through the aromatic rings are given in Table 3.9, and show that rings 3 and 4 are subject to the greatest distortion. Rings 2 and 5 also show significant deviations from planarity, but rings 1 and 6 are planar within the limits of experimental error. The dihedral angles between successive mean planes (Table 3.10) show the same trend, although the differences in the angles are not statistically significant.

A view of the hexahelicene molecule showing its helical structure is given in Figure 3.3. The intramolecular non-bonded C...C contacts which define the pitch of the helix are given in

Table 3.11. The shortest such contacts are C(1)...C(22) and the symmetrically-related C(21)...C(26); both are 2.966(13)Å, and compare well with the value predicted from theoretical calculations[8] of 3.004Å.

The dimensions of the two BTNF molecules do not differ significantly from those determined by Pollard[9]. The two benzene rings of each molecule are twisted out of the plane of the fluorenone residue in order to relieve the steric strain caused by the juxtaposition of the bromo and nitro groups at the 4 and 5 positions. The nitro groups at the 2 and 7 positions are essentially coplanar with their respective aromatic rings, whereas the 5-nitro group is forced out of coplanarity with the aromatic ring because of the proximity of the 4-bromo group. The equations of the mean planes of the C-nitro groups and of the aromatic rings in the BTNF molecules are given in Table 3.12, while the dihedral angles between the planes are given in Table 3.13.

References

1. M.S.Newman and D.Lednicer, J.Amer. Chem. Soc., 78, 4765, (1956).

2. I.R.Mackay, J.Monteath Robertson, and J.G.Sime, Chem. Comm., 1470. (1969).

3. D.A.Lightner, D.T.Hefelfinger, T.W.Powers, G.W.Frank and K.N.Trueblood J.Amer. Chem. Soc., 94, (1972).

4. G.W.Franck, D.T.Hefelfinger and D.A.Lightner, Acta Cryst., B29, 223, (1973).

5. M.S.Szwarc and F.Leavitt, J.Amer. Chem. Soc., 78, 3590, (1956).

6. J.N.Murrell, S.F.A.Kettle and J.M.Tedder, VALENCE THEORY, (John Wiley and Sons Ltd., London, 1965), p.261.

7. L.Pauling, THE NATURE OF THE CHEMICAL BOND, (Cornell University Press, Ithaca, New York, 1960), p, 235.

8. M.A.Herraez Zarza and F.Sanchez, Anales Real Soc. españ., Fis. Quim, 61B, 953, (1965).

9. D.R.Pollard, Ph.D. thesis, University of Glasgow (1968).

TABLES AND DIAGRAMS

Table 3.1

Fractional atomic co-ordinates (x 10^5 for bromine and x 10^4 for all other atoms, with standard deviations in parentheses).

	Complex 1			Complex 2		
	x	y	z	x	y	z
Br(1)	57836(12)	4977(5)	23437(7)	59186(14)	8756(7)	64090(8)
Br(2)				76618(60)	15992(26)	80593(31)
N(1)	115(10)	180(5)	2457(7)	217(12)	213(6)	6000(7)
N(2)	7932(10)	4464(4)	4413(5)	7335(12)	4228(6)	10049(6)
N(3)	7283(8)	1955(4)	2397(5)			
O(1)	93(11)	-421(5)	1970(8)	388(11)	-355(5)	5511(7)
O(2)	-893(8)	390(5)	2761(7)	-952(11)	375(8)	6162(8)
O(3)	2574(9)	2975(4)	4442(5)	1895(7)	2970(4)	8393(4)
O(4)	7415(11)	4931(4)	4909(5)	8598(12)	4246(6)	10262(6)
O(5)	9100(9)	4543(4)	4207(5)	6656(13)	4723(6)	10294(6)
O(6)	8427(11)	1926(5)	2489(7)			
O(7)	6418(11)	1698(5)	1834(6)			
C(1)	7392(8)	3618(4)	5926(4)	3775(10)	2810(6)	1995(5)
C(2)	8695(9)	3980(5)	5833(5)	2386(13)	2613(8)	2204(7)
C(3)	9644(10)	3595(5)	5360(5)	1761(14)	3113(9)	2736(9)
C(4)	9256(10)	2857(6)	4964(5)	2425(15)	3763(9)	3091(8)
C(5)	7943(10)	2477(5)	5024(5)	3858(18)	4051(7)	2944(7)
C(6)	7447(13)	1711(5)	4523(6)	4622(24)	4727(8)	3385(8)

Table 3.1 (cont'd)

	x	y	z	x	y	z
C(7)	6098(11)	1368(5)	4501(6)	5937(20)	4922(7)	3278(8)
C(8)	5118(10)	1746(5)	5013(5)	6709(14)	4482(9)	2721(10)
C(9)	3615(11)	1377(5)	4902(6)	8128(22)	4666(13)	2657(12)
C(10)	2672(11)	1757(6)	5328(6)	8868(13)	4221(10)	2239(10)
C(11)	3156(9)	2451(5)	5969(5)	8254(27)	3521(12)	1653(12)
C(12)	2114(10)	2827(6)	6402(6)	8764(19)	2944(16)	1151(16)
C(13)	2584(10)	3484(6)	7025(6)	8256(19)	2324(11)	620(10)
C(14)	4067(9)	3751(5)	7326(5)	6676(22)	2173(11)	404(10)
C(15)	4508(11)	4406(5)	8047(5)	5943(35)	1563(12)	-179(12)
C(16)	5917(12)	4654(5)	8380(6)	4435(37)	1350(8)	-533(8)
C(17)	6998(9)	4233(5)	8079(5)	3546(22)	1975(8)	-226(8)
C(18)	8445(11)	4436(6)	8490(6)	2114(20)	1985(9)	-511(8)
C(19)	9435(10)	3972(6)	8264(6)	1539(17)	2503(11)	-295(8)
C(20)	8969(9)	3291(5)	7634(5)	2330(12)	3214(8)	315(7)
C(21)	7618(9)	3081(5)	7196(5)	3672(10)	3249(5)	648(5)
C(22)	6606(8)	3560(8)	7397(5)	4395(13)	2645(5)	427(5)
C(23)	5124(8)	3358(4)	6950(5)	5845(14)	2695(7)	792(8)
C(24)	4682(8)	2764(4)	6173(5)	6565(11)	3282(8)	1472(8)
C(25)	5611(9)	2457(4)	5606(5)	5936(11)	3746(6)	2142(7)
C(26)	6977(8)	2860(4)	5544(5)	4535(11)	3530(5)	2333(5)
C(27)	4103(10)	909(5)	2603(6)	4130(9)	1068(5)	6770(6)
C(28)	2761(12)	455(5)	2411(7)	2842(11)	581(6)	6293(7)

Table 3.1 (cont'd)

	x	y	z	x	y	z
C(29)	1570(9)	701(5)	2683(6)	1533(10)	779(6)	6499(7)
C(30)	1611(9)	1403(5)	3232(6)	1384(10)	1418(6)	7097(7)
C(31)	2940(9)	1863(4)	3390(5)	2657(9)	1864(5)	7561(6)
C(32)	3361(11)	2643(5)	3989(6)	2824(10)	2626(6)	8194(6)
C(33)	4846(9)	2896(4)	3925(5)	4383(10)	2842(5)	8516(5)
C(34)	5653(10)	3592(4)	4279(5)	5078(11)	3480(5)	9148(6)
C(35)	7007(10)	3709(5)	4053(6)	6522(11)	3535(5)	9376(5)
C(36)	7562(10)	3186(5)	3480(6)	7285(10)	2980(5)	9063(5)
C(37)	6679(9)	2486(5)	3102(5)	6528(10)	2339(5)	8443(6)
C(38)	5350(8)	2314(4)	3331(5)	5105(8)	2262(4)	8114(5)
C(34)	4193(8)	1656(4)	3057(5)	4043(9)	1691(5)	7456(5)

Assumed coordinates of the disordered nitro group.

N(3)	7321	1786	8277	Population parameter = 0.69
O(6)	8574	1818	8234	
O(7)	6587	1149	8105	
N(3')	5357	0857	6340	Population parameter = 0.31
O(6')	6536	1321	6511	
O(7')	4714	0179	6064	

Table 3.2

Anisotropic thermal parameters (Uij x 10^4 for bromine, Uij x 10^3 for all other atoms). Standard deviations are in parentheses.

Complex 1

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	686(7)	561(5)	928(8)	161(4)	168(5)	153(4)
N(1)	53(5)	80(5)	121(7)	-6(4)	-12(4)	44(4)
N(2)	89(6)	58(4)	54(4)	-10(3)	-19(4)	25(2)
N(3)	35(4)	60(4)	83(5)	-4(3)	14(3)	21(3)
O(1)	83(6)	77(5)	183(10)	-28(4)	4(4)	17(5)
O(2)	46(4)	96(5)	180(8)	0(3)	6(4)	55(4)
O(3)	83(4)	69(5)	93(5)	28(3)	40(3)	24(3)
O(4)	129(7)	56(4)	80(5)	-9(4)	-14(4)	28(3)
O(5)	91(5)	79(4)	81(5)	-42(4)	-13(4)	36(3)
O(6)	86(6)	85(5)	153(8)	26(4)	23(5)	28(5)
O(7)	114(6)	105(5)	107(5)	49(4)	62(3)	56(3)
C(1)	43(4)	40(3)	38(4)	0(3)	-4(3)	11(2)
C(2)	43(5)	60(4)	43(4)	-6(3)	-2(3)	21(3)
C(3)	42(5)	75(5)	51(5)	1(4)	6(3)	17(3)
C(4)	47(5)	79(5)	52(5)	13(4)	8(3)	19(3)
C(5)	58(5)	48(4)	50(5)	11(3)	13(3)	20(3)
C(6)	101(8)	55(5)	46(5)	24(5)	10(5)	12(4)
C(7)	67(6)	56(5)	53(5)	4(4)	2(4)	8(3)

Table 3.2 (cont'd)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(8)	60(5)	47(4)	41(4)	-4(3)	-8(3)	13(3)
C(9)	78(6)	53(4)	49(5)	-21(4)	-15(4)	20(3)
C(10)	59(6)	78(5)	56(5)	-11(4)	-9(4)	36(3)
C(11)	46(5)	68(4)	42(4)	-2(3)	-2(3)	30(3)
C(12)	53(5)	97(5)	66(5)	7(4)	6(3)	49(3)
C(13)	52(5)	92(5)	73(5)	24(4)	17(3)	58(3)
C(14)	43(5)	72(4)	56(4)	21(3)	127(3)	40(2)
C(15)	73(6)	65(5)	42(4)	26(4)	5(4)	27(3)
C(16)	79(7)	55(4)	59(5)	23(4)	22(4)	26(3)
C(17)	57(5)	59(4)	36(4)	7(3)	3(3)	18(2)
C(18)	62(6)	67(6)	47(5)	-11(4)	-6(4)	15(4)
C(19)	44(5)	75(5)	64(5)	2(4)	3(4)	23(3)
C(20)	40(5)	63(4)	58(5)	9(3)	3(3)	22(3)
C(21)	39(4)	59(4)	42(4)	14(3)	8(3)	24(2)
C(22)	43(4)	45(3)	42(4)	5(3)	3(3)	24(2)
C(23)	34(4)	51(4)	46(4)	9(3)	6(3)	24(2)
C(24)	40(4)	51(3)	44(4)	2(3)	0(3)	22(2)
C(25)	51(5)	41(3)	37(4)	-3(3)	-6(3)	12(2)
C(26)	43(4)	40(3)	39(4)	8(3)	5(3)	15(2)
C(27)	49(5)	64(5)	80(6)	14(3)	15(4)	28(3)
C(28)	65(6)	45(4)	91(6)	-6(4)	0(5)	17(3)
C(29)	41(5)	55(4)	90(6)	-7(3)	0(4)	30(3)
C(30)	41(5)	55(4)	71(5)	5(3)	6(3)	25(3)
C(31)	51(5)	46(4)	53(4)	7(3)	9(3)	18(3)

Table 3.2 (cont'd)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(32)	63(6)	52(4)	62(5)	10(4)	14(4)	23(3)
C(33)	51(5)	39(3)	40(4)	3(3)	-3(3)	9(3)
C(34)	63(5)	42(4)	48(4)	0(3)	-4(4)	13(3)
C(35)	65(6)	49(4)	55(5)	-11(3)	-16(4)	23(3)
C(36)	48(5)	54(4)	67(5)	-2(3)	0(4)	26(3)
C(37)	41(5)	54(4)	49(5)	5(3)	9(3)	17(3)
C(38)	36(4)	43(4)	48(4)	0(3)	4(3)	11(3)
C(39)	44(4)	38(3)	47(4)	0(3)	2(3)	15(2)

Complex 2

Br(7)	46(7)	51(7)	67(9)	7(5)	9(5)	12(6)
Br(2)	69(6)	56(5)	93(8)	16(4)	17(5)	15(4)
N(1)	75(7)	98(7)	105(8)	-5(5)	2(5)	35(5)
N(2)	98(7)	89(6)	62(5)	-2(5)	0(4)	26(3)
O(1)	93(6)	88(6)	145(9)	-18(4)	-27(5)	14(5)
O(2)	62(6)	200(13)	131(9)	0(6)	-7(5)	-2(9)
O(3)	62(4)	89(4)	85(4)	35(3)	22(3)	48(2)
O(4)	106(7)	110(7)	81(6)	-6(5)	-22(5)	10(5)
O(5)	146(9)	93(6)	83(6)	27(6)	14(5)	-5(5)
C(1)	57(6)	80(5)	46(5)	13(4)	2(3)	27(3)
C(2)	64(7)	119(8)	74(6)	1(5)	8(4)	58(4)
C(3)	72(7)	147(10)	92(8)	39(6)	23(5)	63(5)

Table 3.2 (cont'd)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(4)	87(8)	143(10)	91(8)	65(7)	38(5)	58(5)
C(5)	153(12)	68(6)	60(7)	24(7)	-34(6)	18(4)
C(6)	221(19)	89(7)	75(7)	42(9)	-15(9)	33(5)
C(7)	164(14)	65(6)	65(6)	10(7)	-22(7)	19(4)
C(8)	74(7)	137(7)	152(8)	-26(5)	-38(5)	117(3)
C(9)	138(14)	205(11)	149(9)	-10(8)	-24(8)	142(4)
C(10)	49(7)	163(10)	134(9)	-24(5)	-20(5)	99(5)
C(11)	208(19)	156(11)	109(10)	79(11)	40(10)	102(5)
C(12)	197(20)	237(15)	166(13)	76(12)	33(11)	165(6)
C(13)	125(9)	192(11)	130(8)	109(8)	83(5)	118(5)
C(14)	170(13)	143(10)	109(8)	78(9)	75(7)	93(5)
C(15)	346(26)	160(11)	101(9)	119(13)	109(10)	10(5)
C(16)	437(36)	63(7)	49(7)	19(12)	47(10)	8(5)
C(17)	203(15)	76(7)	71(6)	7(8)	49(7)	32(4)
C(18)	162(14)	108(10)	55(7)	-61(10)	-8(8)	21(6)
C(19)	97(10)	191(14)	64(7)	-47(9)	-4(6)	59(5)
C(20)	60(7)	135(8)	57(5)	-9(5)	0(4)	47(4)
C(21)	54(5)	71(5)	45(4)	10(3)	5(3)	27(3)
C(22)	105(8)	61(5)	37(4)	-5(4)	8(4)	21(3)
C(23)	100(7)	96(6)	92(6)	53(5)	56(4)	66(3)
C(24)	36(5)	133(7)	117(7)	7(4)	9(4)	96(3)
C(25)	64(6)	67(5)	79(6)	-5(4)	-16(4)	44(3)
C(26)	72(6)	61(4)	38(4)	22(4)	0(4)	16(3)
C(27)	35(5)	63(4)	72(5)	17(3)	17(3)	35(3)

Table 3.2 (cont'd)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(28)	50(6)	69(5)	92(6)	-9(4)	-2(4)	32(4)
C(29)	26(5)	87(6)	84(6)	-8(4)	-7(4)	35(4)
C(30)	45(5)	75(5)	85(6)	10(4)	13(4)	35(4)
C(31)	44(5)	67(4)	67(5)	5(3)	8(3)	34(3)
C(32)	46(5)	73(4)	67(5)	21(3)	19(3)	45(3)
C(33)	59(5)	60(4)	54(4)	16(3)	16(3)	31(2)
C(34)	73(6)	62(4)	55(5)	9(4)	14(4)	26(3)
C(35)	74(6)	56(5)	42(5)	-2(4)	5(4)	12(3)
C(36)	57(6)	69(5)	45(5)	-3(4)	-7(3)	22(3)
C(37)	57(5)	64(4)	63(5)	19(3)	14(3)	34(3)
C(38)	29(4)	51(4)	62(4)	8(3)	7(3)	24(2)
C(39)	46(5)	53(4)	64(4)	9(3)	4(3)	31(2)

Temperature factors assigned to the disordered nitro group.

	U_{iso} ($\times 10^3$).
N(3)	48
O(6)	82
O(7)	82
N(3')	48
O(6')	82
O(7')	82

Table 3.3

Hydrogen atom positions (x, y, z x 10^3) calculated assuming a C-H distance of 1.09 Å. Each hydrogen atom has the same number as the carbon atom to which it is bound.

Complex 1

	x	y	z		x	y	z
H(1)	667	394	630	H(2)	898	457	611
H(3)	1069	389	532	H(4)	1009	257	458
H(6)	823	140	419	H(7)	514	79	410
H(9)	326	81	447	H(10)	152	153	518
H(12)	93	258	623	H(13)	178	380	727
H(15)	369	471	834	H(16)	627	519	891
H(18)	877	497	901	H(19)	1057	414	858
H(20)	969	290	751	H(21)	732	256	670
H(28)	268	-16	202	H(30)	54	147	340
H(34)	524	404	472	H(36)	864	331	332

Complex 2

	x	y	z		x	y	z
H(1)	423	239	153	H(2)	183	204	192
H(3)	66	295	287	H(4)	187	415	353
H(6)	410	514	384	H(7)	654	547	368

Table 3.3 (cont'd)

	x	y	z		x	y	z
H(9)	865	523	298	H(10)	1006	441	234
H(12)	999	304	126	H(13)	898	195	36
H(15)	658	159	1032	H(16)	408	82	901
H(18)	145	147	904	H(19)	110	282	1024
H(20)	169	323	-18	H(21)	425	377	112
H(28)	288	7	576	H(30)	31	157	719
H(34)	449	397	943	H(36)	843	303	929

Table 3.4

Observed Structure Amplitudes and Calculated Structure Factors

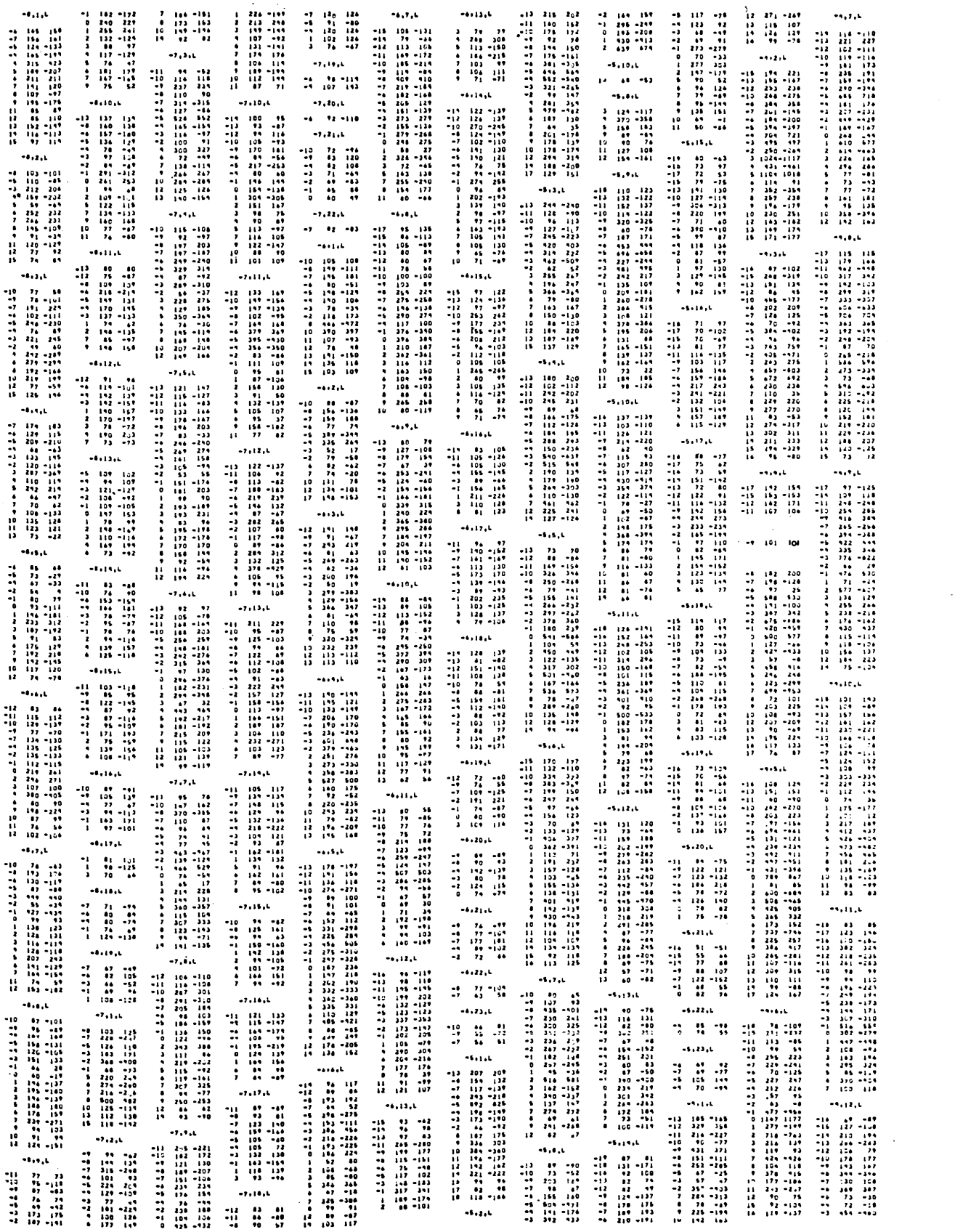


Table 3.4 (cont'd)

Table 3.4 (cont'd)

Table 3.4 (cont'd)

Table 3.5

Intermolecular C...C contacts less than 3.5Å between the hexahelicene and BTNF molecules. Standard deviations are in parentheses.

(a) Between hexahelicene (Complex 2) and BTNF (Complex 1).

C(1) ..... C(38)	3.425(16)	C(3) ..... C(32)	3.268(23)
C(2) ..... C(31)	3.272(21)	C(5) ..... C(34)	3.463(20)

(b) Between hexahelicene (Complex 1) and BTNF (Complex 1).

C(1) ..... C(34)	3.390(13)	C(4) ..... C(36)	3.489(17)
C(2) ..... C(35)	3.401(14)	C(7) ..... C(39)	3.464(15)
C(3) ..... C(35)	3.472(15)	C(9) ..... C(31)	3.455(16)

(c) Between hexahelicene (Complex 1) and BTNF (Complex 2).

C(13) .... C(32)	3.380(19)	C(17) .... C(35)	3.347(16)
C(14) .... C(32)	3.471(17)	C(18) .... C(35)	3.385(17)
C(15) .... C(34)	3.431(18)	C(19) .... C(36)	3.497(17)
C(16) .... C(34)	3.333(18)	C(20) .... C(36)	3.444(15)
C(17) .... C(34)	3.456(16)	C(21) .... C(37)	3.436(16)

(d) Between hexahelicene (Complex 2) and BTNF (Complex 2).

C(18) ..... C(32)	3.291(21)	C(19) .... C(32)	3.257(22)
		C(21) .... C(34)	3.379(16)

Table 3.6

Bond lengths ($\mathring{A}$), with standard deviations in parentheses.

	Complex 1	Complex 2
C(1) - C(2)	1.385(12)	1.426(16)
C(2) - C(3)	1.387(13)	1.341(19)
C(3) - C(4)	1.360(13)	1.252(21)
C(4) - C(5)	1.386(14)	1.468(22)
C(5) - C(6)	1.439(12)	1.338(18)
C(6) - C(7)	1.333(15)	1.284(28)
C(7) - C(8)	1.438(13)	1.392(21)
C(8) - C(9)	1.443(13)	1.344(25)
C(9) - C(10)	1.341(15)	1.261(27)
C(10) - C(11)	1.412(11)	1.400(23)
C(11) - C(12)	1.416(14)	1.349(35)
C(12) - C(13)	1.351(13)	1.241(29)
C(13) - C(14)	1.391(12)	1.449(26)
C(14) - C(15)	1.436(11)	1.317(25)
C(15) - C(16)	1.340(14)	1.433(43)
C(16) - C(17)	1.418(14)	1.561(32)
C(17) - C(18)	1.418(13)	1.411(28)
C(18) - C(19)	1.385(15)	1.194(28)
C(19) - C(20)	1.385(11)	1.470(19)
C(20) - C(21)	1.360(11)	1.338(15)

Table 3.6 (cont'd)

	Complex 1	Complex 2
C(21) - C(22)	1.420(12)	1.425(16)
C(22) - C(17)	1.414(9)	1.471(15)
C(22) - C(23)	1.471(11)	1.444(18)
C(23) - C(14)	1.405(12)	1.399(24)
C(23) - C(24)	1.443(9)	1.378(15)
C(24) - C(11)	1.421(11)	1.543(26)
C(24) - C(25)	1.418(11)	1.451(16)
C(25) - C(8)	1.401(9)	1.480(16)
C(25) - C(26)	1.451(11)	1.430(15)
C(26) - C(5)	1.439(12)	1.463(16)
C(26) - C(1)	1.395(10)	1.391(13)
Br(1) - C(27)	1.885(10)	1.874(9)
Br(2) - C(37)		1.903(12)
N(1) - C(29)	1.506(12)	1.497(12)
N(1) - O(1)	1.190(13)	1.189(14)
N(1) - O(2)	1.174(14)	1.206(16)
N(2) - C(35)	1.502(11)	1.500(11)
N(2) - O(4)	1.216(12)	1.207(16)
N(2) - O(5)	1.189(13)	1.221(17)
N(3) - C(37)	1.531(11)	
N(3) - O(6)	1.082(13)	
N(3) - O(7)	1.159(12)	
O(3) - C(32)	1.215(13)	1.181(12)
C(27) - C(28)	1.367(13)	1.411(11)
C(28) - C(29)	1.332(14)	1.371(14)

Table 3.6 (cont'd)

	Complex 1	Complex 2
C(29) - C(30)	1.375(11)	1.362(14)
C(30) - C(31)	1.369(11)	1.370(11)
C(31) - C(32)	1.498(10)	1.498(12)
C(32) - C(33)	1.433(13)	1.460(12)
C(33) - C(34)	1.369(10)	1.377(11)
C(34) - C(35)	1.375(14)	1.357(15)
C(35) - C(36)	1.363(13)	1.377(14)
C(36) - C(37)	1.403(11)	1.387(11)
C(37) - C(38)	1.381(12)	1.382(12)
C(38) - C(33)	1.423(10)	1.417(12)
C(38) - C(39)	1.471(10)	1.472(10)
C(39) - C(31)	1.398(12)	1.393(13)
C(39) - C(27)	1.398(12)	1.407(11)

Table 3.7

Bond angles (degrees), with standard deviations in parentheses.

	Complex 1	Complex 2
C(26) - C(1) - C(2)	121.6(0.7)	121.4(0.9)
C(1) - C(2) - C(3)	120.7(0.8)	121.3(1.2)
C(2) - C(3) - C(4)	119.1(0.9)	120.3(1.4)
C(3) - C(4) - C(5)	121.9(0.9)	124.8(1.3)
C(4) - C(5) - C(6)	120.0(0.7)	116.4(1.0)
C(26) - C(5) - C(6)	118.3(0.8)	119.3(1.5)
C(4) - C(5) - C(6)	121.5(0.9)	123.9(1.4)
C(5) - C(6) - C(7)	121.4(1.0)	120.9(1.6)
C(6) - C(7) - C(8)	120.7(0.8)	125.7(1.2)
C(7) - C(8) - C(25)	120.7(0.8)	118.8(1.2)
C(25) - C(8) - C(9)	120.7(0.8)	115.8(1.4)
C(7) - C(8) - C(9)	118.6(0.7)	125.5(1.4)
C(8) - C(9) - C(10)	118.2(0.8)	124.1(1.9)
C(9) - C(10) - C(11)	121.8(0.8)	124.1(1.6)
C(10) - C(11) - C(24)	119.7(0.8)	118.8(1.8)
C(24) - C(11) - C(12)	120.8(0.7)	104.9(1.6)
C(10) - C(11) - C(12)	119.5(0.8)	136.4(2.2)
C(11) - C(12) - C(13)	119.3(0.8)	138.1(2.5)
C(12) - C(13) - C(14)	121.5(0.9)	114.2(2.1)
C(13) - C(14) - C(23)	120.1(0.7)	120.7(1.4)

Table 3.7 (cont'd)

	Complex 1	Complex 2
C(23) - C(14) - C(15)	120.0(0.7)	116.0(2.1)
C(14) - C(15) - C(16)	121.4(0.9)	131.3(2.5)
C(15) - C(16) - C(17)	120.7(0.8)	114.0(1.4)
C(16) - C(17) - C(22)	120.0(0.7)	112.9(1.6)
C(22) - C(17) - C(18)	118.5(0.8)	118.0(1.4)
C(17) - C(18) - C(19)	121.4(0.8)	125.9(1.3)
C(18) - C(19) - C(20)	118.4(0.8)	120.5(1.5)
C(19) - C(20) - C(21)	122.7(0.9)	117.9(1.4)
C(20) - C(21) - C(22)	119.8(0.7)	123.8(0.9)
C(21) - C(22) - C(17)	118.9(0.7)	113.7(1.2)
C(17) - C(22) - C(23)	118.8(0.7)	123.3(1.2)
C(21) - C(22) - C(23)	122.2(0.6)	123.0(0.8)
C(22) - C(23) - C(14)	117.3(0.6)	119.9(1.1)
C(14) - C(23) - C(24)	118.6(0.7)	115.7(1.3)
C(22) - C(23) - C(24)	124.1(0.7)	123.9(1.2)
C(23) - C(24) - C(11)	115.9(0.7)	123.2(1.2)
C(11) - C(24) - C(25)	117.4(0.6)	108.6(1.0)
C(23) - C(24) - C(25)	126.7(0.7)	128.1(1.0)
C(24) - C(25) - C(8)	118.6(0.7)	123.3(1.1)
C(8) - C(25) - C(26)	117.0(0.7)	112.9(1.0)
C(24) - C(25) - C(26)	124.0(0.6)	123.8(0.8)
C(25) - C(26) - C(5)	119.6(0.6)	121.5(0.9)
C(5) - C(26) - C(1)	116.5(0.7)	115.5(1.0)
C(25) - C(26) - C(1)	123.8(0.7)	122.9(0.9)
C(39) - C(27) - C(28)	118.5(0.9)	120.6(0.8)

Table 3.7 (cont'd)

	Complex 1	Complex 2
C(27) - C(28) - C(29)	121.6(0.8)	116.5(0.9)
C(28) - C(29) - C(30)	123.3(0.8)	125.4(0.8)
C(29) - C(30) - C(31)	114.3(0.8)	116.1(0.9)
C(30) - C(31) - C(39)	124.8(0.7)	123.7(0.8)
C(39) - C(31) - C(32)	107.8(0.7)	109.1(0.7)
C(30) - C(31) - C(32)	127.1(0.8)	126.9(0.9)
C(31) - C(32) - C(33)	106.5(0.8)	104.7(0.8)
C(32) - C(33) - C(38)	108.9(0.6)	109.5(0.6)
C(38) - C(33) - C(34)	122.2(0.8)	123.0(0.9)
C(32) - C(33) - C(34)	128.4(0.8)	127.4(0.9)
C(33) - C(34) - C(35)	117.2(0.8)	116.6(0.9)
C(34) - C(35) - C(36)	124.4(0.8)	124.4(0.8)
C(35) - C(36) - C(37)	117.0(0.9)	116.8(0.9)
C(36) - C(37) - C(38)	122.0(0.8)	122.7(0.9)
C(37) - C(38) - C(33)	116.9(0.7)	115.8(0.7)
C(33) - C(38) - C(39)	107.9(0.7)	107.7(0.7)
C(37) - C(38) - C(39)	135.0(0.7)	136.3(0.8)
C(38) - C(39) - C(31)	108.0(0.6)	107.7(0.7)
C(31) - C(39) - C(27)	116.2(0.7)	116.7(0.7)
C(39) - C(27) - Br(1)	122.3(0.6)	122.5(0.6)
Br(1) - C(27) - C(28)	118.8(0.8)	116.8(0.7)
C(28) - C(29) - N(1)	119.8(0.8)	113.5(0.9)
C(29) - N(1) - O(1)	115.6(1.0)	119.3(1.0)

Table 3.7 (cont'd)

	Complex 1	Complex 2
C(29) - N(1) - O(2)	119.0(0.8)	115.0(1.0)
O(1) - N(1) - O(2)	125.4(1.0)	125.6(1.1)
N(1) - C(29) - C(30)	116.6(0.8)	121.2(0.9)
C(31) - C(32) - O(3)	125.2(0.9)	127.5(0.8)
O(3) - C(32) - C(33)	128.3(0.7)	127.8(0.8)
C(34) - C(35) - N(2)	119.6(0.8)	118.5(0.9)
C(35) - N(2) - O(4)	115.7(0.9)	116.8(1.0)
C(35) - N(2) - O(5)	117.7(0.8)	115.7(1.0)
O(4) - N(2) - O(5)	126.5(0.8)	127.4(1.0)
N(2) - C(35) - C(36)	116.0(0.9)	117.0(0.9)
C(36) - C(37) - N(3)	114.0(0.8)	
C(37) - N(3) - O(6)	116.7(0.8)	
C(37) - N(3) - O(7)	111.1(0.8)	
O(6) - N(3) - O(7)	131.8(1.1)	
N(3) - C(37) - C(38)	128.3(0.6)	
C(36) - C(37) - Br(2)		113.8(0.7)
Br(2) - C(37) - C(38)		123.4(0.6)

Table 3.8

Comparison of the mean observed bond lengths (D_{obs}) in the Complex 1 hexahelicene molecule with those obtained from valence-bond ($D_{v.b.}$) and molecular-orbital ($D_{m.o.}$) calculations assuming a planar structure. All bond lengths are in Å, and the atom numbers are those given in Figure 3.1.

Bond	$D_{v.b.}$	$D_{m.o.}$	$D_{obs.}$
1 - 2	1.38	1.39	1.37
2 - 3	1.42	1.41	1.39
3 - 4	1.38	1.39	1.37
4 - 5	1.42	1.41	1.40
5 - 6	1.45	1.42	1.43
6 - 7	1.35	1.38	1.34
7 - 8	1.45	1.42	1.44
8 - 9	1.44	1.42	1.42
9 -10	1.36	1.38	1.35
10 -11	1.44	1.41	1.42
11 -24	1.39	1.42	1.42
24 -25	1.44	1.42	1.43
25 -26	1.45	1.43	1.46
26 - 1	1.42	1.41	1.41
25 - 8	1.38	1.41	1.40
26 - 5	1.41	1.41	1.41

Table 3.9

Mean planes through the aromatic rings of the hexahelicene molecules, together with the root mean square and maximum deviations of the atoms from the planes (Å). The planes are defined by the equation $AX' + BY' + CZ' = D$, where X', Y', and Z' are absolute orthogonal coordinates (in Å), with $X' = ax\sin\beta\sin\gamma^*$, $Y' = -ax\sin\beta\cos\gamma^* + by\sin\alpha$, $Z' = ax\cos\beta + by\cos\alpha$.

Ring	Complex	Deviations		Equation of plane coefficients			
		r.m.s.	max.	A	B	C	D
1	1	0.015	0.022	-0.471	0.175	-0.865	-8.810
1	2	0.016	0.025	-0.462	0.274	-0.843	-1.251
2	1	0.058	0.097	-0.392	0.339	-0.855	-7.648
2	2	0.039	0.066	-0.373	0.400	-0.837	-0.081
3	1	0.074	0.115	-0.205	0.472	-0.858	-6.420
3	2	0.093	0.144	-0.172	0.449	-0.877	1.447
4	1	0.078	0.123	0.016	0.535	-0.845	-5.331
4	2	0.072	0.124	-0.087	0.411	-0.907	3.083
5	1	0.055	0.085	0.210	0.489	-0.847	-4.887
5	2	0.064	0.107	0.299	0.312	-0.902	4.014
6	1	0.024	0.033	0.342	0.342	-0.875	-5.283
6	2	0.020	0.030	0.388	0.173	-0.905	3.882

Table 3.10

Dihedral angles (degrees) between the mean planes through the aromatic rings of the hexahelicene molecules.

Between rings:	Complex	Angle
1 and 2	1	10.5
1 and 2	2	8.8
2 and 3	1	13.2
2 and 3	2	12.1
3 and 4	1	13.2
3 and 4	2	15.1
4 and 5	1	11.4
4 and 5	2	13.5
5 and 6	1	11.4
5 and 6	2	9.5

Table 3.11

Intramolecular non-bonded C...C contacts (Å) in the hexahelicene molecules, with standard deviations in parentheses.

Contact	Complex 1	Complex 2
C(1) ..... C(22)	2.966(13)	2.942(15)
C(1) ..... C(23)	3.090(12)	3.029(18)
C(1) ..... C(21)	3.046(14)	3.039(17)
C(21) .... C(26)	2.966(13)	3.015(14)
C(21) .... C(25)	3.075(11)	3.099(14)

Table 3.12

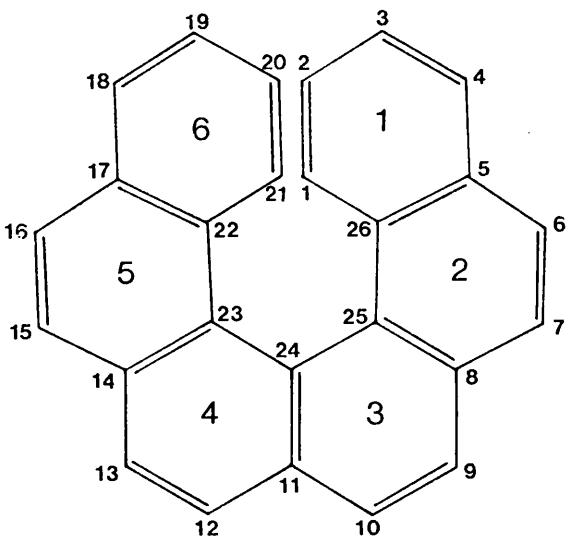
Mean planes through the aromatic rings and C-nitro groups of the BTNF molecules, together with the root mean square deviations (Δ) of the atoms from the planes. The planes are defined by the equation $AX' + BY' + CZ' = D$, where X', Y', and Z' are absolute orthogonal coordinates (in A), with $X' = a x \sin\beta \sin\gamma^*$, $Y' = -a x \sin\beta \cos\gamma^* + b y \sin\alpha$, $Z' = a x \cos\beta + b y \cos\alpha + c z$.

Plane	Complex	Δ(Å)	Equation of plane coefficients			
			A	B	C	D
Ring 1	1	0.043	-0.239	0.233	-0.943	-4.283
Ring 1	2	0.038	0.002	0.479	-0.876	-9.397
Ring 2	1	0.039	-0.325	0.318	-0.891	-4.088
Ring 2	2	0.032	0.148	0.394	-0.907	-9.757
Ring 3	1	0.019	-0.438	0.310	-0.844	-4.416
Ring 3	2	0.029	0.291	0.326	-0.900	-9.377
C(29)-NO_2	1	0.001	-0.250	0.325	-0.912	-4.008
C(29)-NO_2	2	0.008	0.004	0.390	-0.921	-10.133
C(35)-NO_2	1	0.007	-0.425	0.278	-0.861	-4.600
C(35)-NO_2	2	0.010	0.314	0.271	-0.910	-9.648
C(37)-NO_2	1	0.017	0.300	0.708	-0.640	2.129
C(37)-NO_2	2	0.013	-0.159	-0.174	-0.972	-14.658

Table 3.13

Dihedral angles (degrees) between the mean planes of the aromatic rings and C-nitro groups of the BTNF molecules.

Planes	Dihedral angle	
	Complex 1	Complex 2
Ring 1 - Ring 2	7.5	7.1
Ring 2 - Ring 3	7.1	9.1
C(29)-NO_2 - Ring 1	5.5	6.4
C(35)-NO_2 - Ring 3	2.5	2.9
C(37)-NO_2 - Ring 3	51.1	39.4



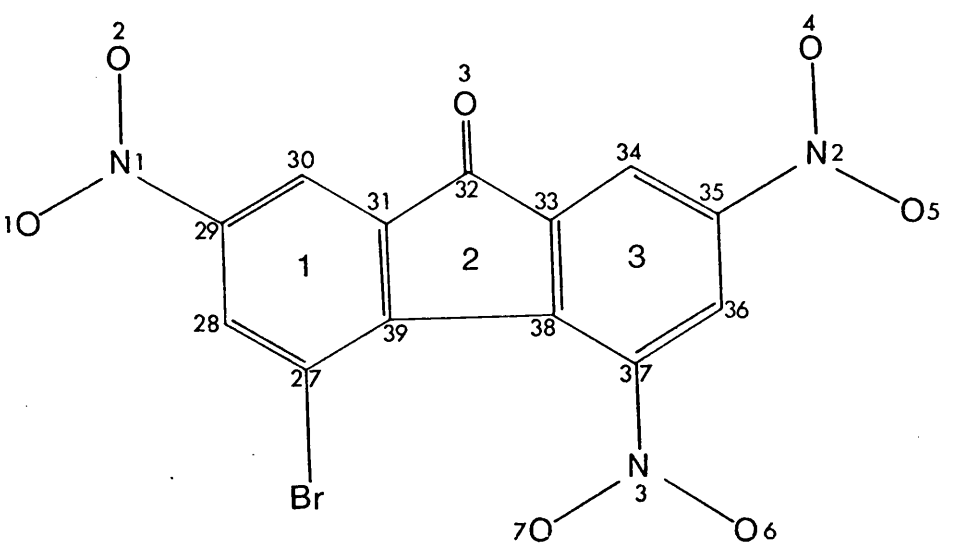


Figure 3.1 : The numbering system applied to the hexahelicene and BTNF molecules.

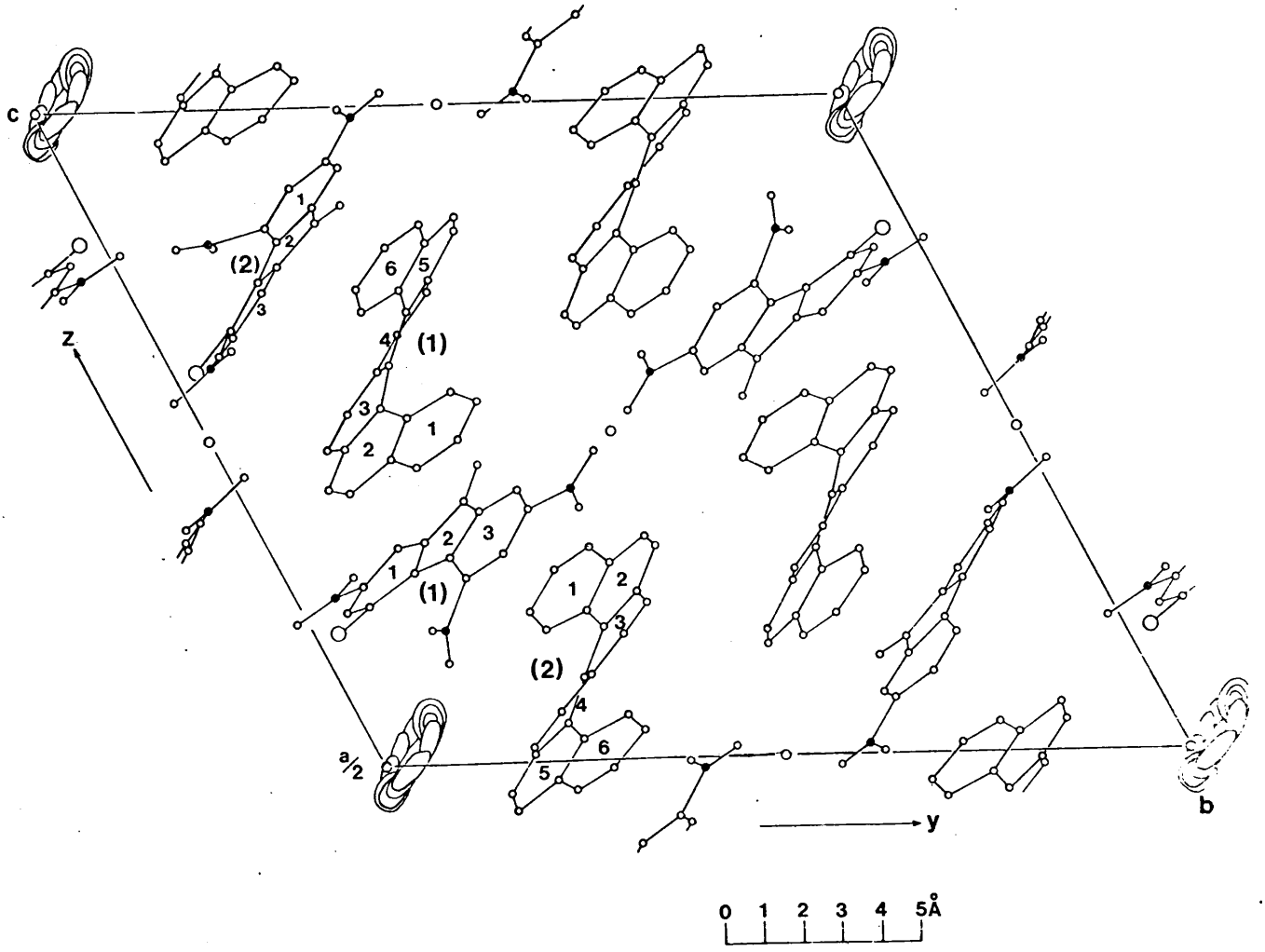


Figure 3.2: The crystal structure projected along the a* axis. The complex 1 and 2 molecules are labelled(1)and(2)respectively.

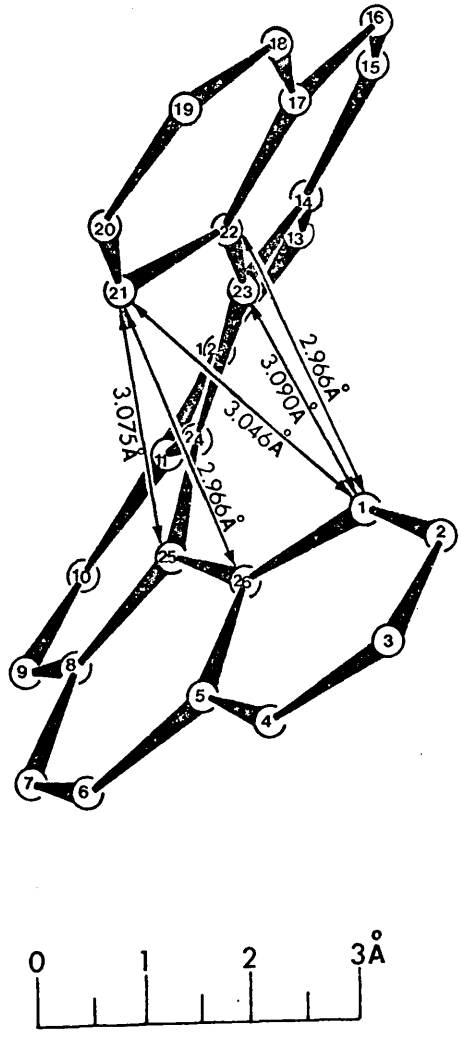


Figure 3.3: The Complex 1 hexahelicene molecule viewed along a*, showing the shortest intramolecular contacts.

CHAPTER 4

THE CRYSTAL AND MOLECULAR STRUCTURES OF THE 'SUPER-ACID' SALTS

POTASSIUM TRI-HYDROGEN DI-SUCCINATE AND POTASSIUM TRI-HYDROGEN DI-GLUTARATE

4.1. Introduction

The acid salts of carboxylic acids

Many monobasic carboxylic acids readily form crystalline acid salts of composition $\underline{M}\underline{H}\underline{X}_2$, where $\underline{M}$ is a univalent cation, and $\underline{H}\underline{X}$ is the free acid (R.COOH). It has been shown, as a result of x-ray and neutron diffraction studies of a number of these acid salts, that they can be classified into two structural types, A and B.[1] In type A the two acidic residues are equivalent, linked by a very short O···H···O bond across a crystallographic element of symmetry, and the structure may be formulated as $\underline{M}^+(\underline{X}\underline{H}\underline{X})^-$. Crystals of this type of acid salt have anomalous infra-red spectra,[2] the most notable features being the absence of an O-H stretching band above 1700 cm^{-1}, and a broad band of absorption below 1600 cm^{-1}.

Type B acid salts have crystal structures in which the crystallographically distinct anion $\underline{X}^-$ and free acid $\underline{H}\underline{X}$ can be recognised, so that the structure may be formulated as $\underline{M}^+.\underline{X}^-.\underline{H}\underline{X}$. The acid residues are joined by a short hydrogen bond, but in this case the oxygen atoms involved are not symmetry-related. The infra-red spectra of Type B acid salts approximate to a superposition of the spectra of the free acid and its anion.

Dicarboxylic acids ($\underline{H_2Y}$) form acid salts ($\underline{M}\underline{H}\underline{Y}$) which can also be classified into two structural types. Type $\underline{A_2}$ acid salts, in which the two carboxyl groups are crystallographically equivalent, each being effectively half-ionised, are analogous to Type A acid salts of monobasic

carboxylic acids and have the same type of anomalous infra-red spectra. In Type $\underline{B}_2$ salts, the carboxyl groups are differentiated, one being ionised, the other not; this type is thus analogous to Type $\underline{B}$ acid salts of monobasic carboxylic acids, and has a similar infra-red spectrum.

In addition to the normal Type $\underline{A}_2$ and $\underline{B}_2$ acid salts, dicarboxylic acids form 'super-acid' salts of stoichiometric formula $\underline{M}\underline{H}_3\underline{Y}_2$. The crystal structures of the first two members of the series of super-acid salts $\underline{K}\underline{H}_3\underline{Y}_2$, potassium tetroxalate[3] and potassium trihydrogen di-malonate have been investigated by neutron diffraction; as expected (on the basis of their infra-red spectra), both structures contain the unionised acid molecule $\underline{H_2Y}$ and the $\underline{B}_2$ Type acid anion $\underline{HY}^-$. Their structures can thus be more correctly formulated as $\underline{K}^+.\underline{HY}^-.\underline{H_2Y}$. The structure analyses by neutron diffraction of the next two members of the series, potassium tri-hydrogen di-succinate and potassium tri-hydrogen di-glutarate are now described in parts two and three respectively of this chapter.

4.2. The Crystal Structure of Potassium tri-hydrogen di-succinate

4.2.1. Introduction

Potassium tri-hydrogen di-succinate (KH_3Succ_2) was first described by Marshall and Cameron in 1907[5] who studied its morphology during an investigation into crystals with curved boundaries.

Its preparation is simple: equimolar quantities of succinic acid

and potassium hydroxide are dissolved in warm water, and crystals of KH_3Succ_2 separate out on cooling or evaporation. However, although large crystals suitable for neutron diffraction were relatively easy to grow, considerable difficulty was encountered in obtaining small crystals suitable for x-ray analysis - they tended to be split or bent. A full set of neutron diffraction data were therefore collected in the hope that the structure might be solved directly from neutron data. Since potassium is no longer a 'heavy atom' for neutron scattering, an attempt was made to solve the structure by the symbolic addition method, in spite of theoretical objections that the presence of a large number of negatively-scattering hydrogen nuclei make its application invalid. However, the anticipated difficulties were not encountered, and the structure was solved at the first attempt.

4.2.2. Experimental

Crystal Data

The unit-cell parameters were determined from x-ray photographs: $C_8H_{11}O_8K$, M = 2743, monoclinic, a = 7.434(5), b = 18.437(10), c = 9.006(5)Å, β = 109.51(0.1)°; U = 1163.5Å^3, D_m (Marshall and Cameron, 1907) = 1.559, z = 4, D_c = 1.56. Space group, $P2_1/c$ (No. 14).

The goniometric parameters given by Marshall and Cameron correspond to a different choice of axes: $a_G = -a-2c$; $c_G = a$. These lead to the ratios 0.923:1:0.403, 94.7° compared with 0.936:1:0.407, 94.4° cited by Groth.[6]

Data Collection

Diffracted neutron intensities were measured on a Ferranti Mark II automatic diffractometer attached to the Dido reactor at A.E.R.E. (Harwell), using a monochromated neutron beam with $\lambda = 1.172\text{Å}$. The crystal used had dimensions 5.5(parallel to c) x 5 x 3.5 mm^3 and was mounted along c. Integrated intensities were measured for all 1890 independent reflections out to $\theta = 45^\circ$ using $w/2\theta$ scans; of these, 1213 with $|F| \geq 3\sigma(|F|)$ were used in the structure analysis. Absorption corrections were applied to all the data using a calculated μ(effective) of 1.40 cm^{-1}; the incoherent scattering cross-section of hydrogen was taken to be 37.0 x 10^{-24} cm.

Normalised structure amplitudes (E 's) were calculated from the observed structure amplitudes according to the equation

$$E^2 = k^2 F^2_{obs} / e^{-2B(\sin\theta/\lambda)^2} \sum_{j=1}^{N} b_j^2$$

where b_j is the scattering length of the j^{th} atom, and N is the number of atoms in the unit cell. The values of the scale factor k and overall temperature factor B were obtained as follows: the summation of $(E^2-1)^2$ over all reflections was calculated for various physically reasonable values of B, the value of k being adjusted so that the average value of E^2 was forced to be 1.0. The best value of B, and hence k, was taken to be that which minimised the summation $(E^2-1)^2$. These calculations were carried out using the X-RAY SYSTEM program DATFIX; all subsequent programs

used in the structure analysis were also from the X-RAY SYSTEM.

4.2.3 Solution of the phase problem.

The phase problem was solved by an application of the symbolic addition method using the programs SIGMAZ and PHASE, 1,801 Σ_2 relationships were generated by SIGMA2 between the 224 reflections with |E| values greater than 1.5. The reflections 621, $51\bar{7}$, and $43\bar{8}$ were allocated positive signs in order to define an origin before proceeding with the phase determination using the program PHASE. This program finds an initial solution in terms of the top 30-40 percent E 's - in this case 80 were used - which are known as 'generators'. The subset of Σ_2 relationships used in this solution - known as the 'defining' subset - are then tested against the full set of relationships and a count is made of the number of times each relationship in the subset appears 'accordant' or 'discrepant' in terms of all the known relationships. Any relationship in the defining subset which appears discrepant more often than accordant can then be removed from the solution. The program thus finds the most internally self-consistent solution, and this is usually, though not always, the correct one. In the present case, the defining subset contained 77 relationships, of which 1 was subsequently removed to yield a consistent solution. The phases of 206 reflections were determined from this solution, and an E-map computed using these phased E's as coefficients revealed every atom in the structure, including the negatively-scattering hydrogens. Structure factors calculated using the atomic coordinates determined from the E-map gave an R-value of 29

per cent.

It was pointed out in Chapter I that application of the symbolic addition method to diffraction data yields phases for the 'squared structure' - that is, the structure which scatters with the square of the scattering factor for each atom in the original structure. Symbolic addition will thus be successful with neutron data from a structure containing a proportion of negatively-scattering nuclei only if the largest structure factors of the original structure have the same phases as the corresponding structure factors of the squared structure (or of the original structure in which all the nuclei are considered positive scatters), and it was argued that this was likely to be the case when only a moderate proportion of the nuclei were negative scatterers.

Having successfully solved the structure by the symbolic addition method, it was decided to investigate the extent of the agreement between the phases of the original structure and that of the same structure with positively scattering hydrogen nuclei. Structure factors were calculated from the final least-squares parameters using a positive sign for the hydrogen scattering length, and Table 4.2.11. lists these structure factors (F_b+) for the 80 reflections used in the initial symbolic addition solution along with their structure factors calculated using the correct (negative) hydrogen scattering length (F_b-). Although the amplitudes of each pair of F_b+ and F_b- sometimes differ by a large amount, their phases are, without exception, the same, and of the 206 reflections used in the final solution, only 2

have different signs for F_b+ and F_b-. Any errors in the phases determined by the symbolic addition procedure are thus most likely to be the result of differences in the amplitudes of F_b- and F_b+ ; not all of the large F_b-'s correspond to a large F_b+, and since only reflections with a large F_b+ should theoretically be used in the symbolic addition procedure, the reflections for which $F_b+ << F_b-$ have been wrongly (but unavoidably) included. Phases determined for such reflections have a low probability of being correct, and in 8 of the 11 phases which were incorrectly determined in the present analysis (Table 4.2.12), F_b+ is much smaller than F_b- (by 50 per cent or more). This 'amplitude error' effect was not, however, important in this case, since only one of these 'invalid' reflections was among the set of 80 largest reflections from which the initial solution was found.

The proportion of hydrogen scattering power in potassium tri-hydrogen di-succinate is 20 per cent; obviously, neutron data derived from crystals containing increasing proportions of negative scattering nuclei will suffer to an increasing extent from the 'amplitude error' effect amongst the largest structure factors, and the point at which the symbolic addition procedure becomes unworkable is reached, according to Sikka[7] when negative-scattering nuclei account for more than 1/3 of the total scattering power in the unit cell.

4.2.4 Refinement.

The structure was refined by least-squares using the program CRYLSQ.

Nuclear scattering lengths were taken to be 0.35, 0.661, 0.579 and -0.378×10^{-12} cm. for K, C, O and H respectively. Two cycles of full-matrix isotropic least-squares refinement were followed by three cycles of block-diagonal anisotropic least-squares refinement, and convergence was reached with R = 0.086. The weighting scheme used in the last two cycles is defined by the equation $W^{-1} = 1 + [(F_o - 5.0)/3.0]^2$. Seven reflections which seemed to be badly affected by extinction were omitted from the final stages of refinement, and these are listed in Table 4.2.5.

The final positional and vibrational parameters are listed in Tables 4.2.1 and 4.2.2 respectively; the observed structure amplitudes and calculated structure factors are listed in Table 4.2.3 and an analysis of their agreement is given in Table 4.2.4.

4.2.5 Discussion of the structure

The numbering scheme of the crystal-chemical unit (C.C.U.) is shown in Figure 4.2.1; other symmetry-related units needed in the description of the structure are as follows :-

C.C.U. $\underline{x}, \underline{y}, \underline{z}$

I	$-1+\underline{x}, \underline{y}, \underline{z}$	IV	$1+\underline{x}, \underline{y}, 1+\underline{z}$
II	$-\underline{x}, -\underline{y}, -\underline{z}$	V	$\underline{x}, \underline{y}, 1+\underline{z}$
III	$-\underline{x}, -\underline{y}, 1-\underline{z}$	VI	$1-\underline{x}, -\underline{y}, 1-\underline{z}$

The principle bond-lengths and angles in the succinate residues are given

in Table 4.2.6. Figures 4.2.2 and 4.2.3 show the crystal structure projected along the b and c axes respectively.

The two independent succinate residues are clearly differentiated, residue R_1 being the acid anion HY^- and residue R_2 the neutral acid molecule H_2Y. The location of the hydroxylic protons identifies the carboxyl based on C(4) as the carboxylate anion and this is confirmed by a comparison of the differences in C-O bond length and C-C-O angle in the four carboxyl groups (Table 4.2.7). The unionised carboxyls have larger differences in both C-O distance and C-C-O angle than the carboxylate anion.

The main features of the structure are most clearly observed in Figure 4.2.2. The structure consists of infinite chains of the B_2 type residues (R_1) linked head-to-tail along the x-direction by short asymmetric hydrogen bonds, with the neutral acid molecules R_2 attached as festoons: each O(3) atom of the main chain forms a short asymmetric hydrogen bond with O(5)-H of one R_2 residue, and with O(7)-H of the next.

The R_1 residue is in an extended form and its four carbon atoms are coplanar, their mean plane being represented by the equation :

$$0.2471X' + 0.8461Y + 0.4723Z' = 1.843 \text{ Å} ;$$

the root mean square distance of the four atoms from the plane is 0.017 Å. Whereas the R_1 residues fit seven atoms into a primitive translation of 7.43 Å, the R_2 residues have to fit nine atoms into this distance, and in order to allow this, one carboxyl group is in a gauche conformation, with a

dihedral angle of 57.3° about C(6) - C(7). A list of the other important torsion angles in the succinate residues is given in Table 4.2.9.

The interatomic distances and angles in the three hydrogen bonds are given in Table 4.2.10. The O(1) - H···O(4^{I}) and O(5) - H···O(3^{I}) bonds are of similar length, but consideration of their O - H···O angles and H···O distances suggests that the former is the stronger bond. The other hydrogen bond is significantly longer, and its O···O distance of 2.63 Å is similar to those found in carboxylic acid dimers.

Figure 4.2.4 shows the Nakamoto-Margoshes-Rundle relationship[8] between O - H and O···O distances in hydrogen bonds; the curve is that of Hamilton and Ibers[9] representing the best least-squares fit to the O - H and O···O distances of all the O - H···O hydrogen bonds studied by neutron diffraction up to 1967, and shows how the O - H distance tends to increase with decreasing O···O distance. The six points representing the hydrogen bonds in the present analysis and those in potassium tri-hydrogen di-glutarate (Chapter IV, part 3) are plotted in Figure 4.2.4 and fit the Hamilton-Ibers curve very well, considering the average standard deviation in the O - H distances of about 0.016 Å.

The C - H distances have a mean value of 1.089 Å, with an internal standard deviation of 0.025 Å, which suggests that their least-squares standard deviations in Table 4.2.6 are underestimated.

The environment of the potassium ion is shown in Figure 4.2.5. Eight oxygen atoms surround the ion and the six K^{+}···O distances less than 2.84 Å

must be genuine ionic contacts; the two $K^+ \cdots O$ distances of 3.19 Å and 3.28 Å are, however, questionable contacts, although they appear to fill gaps in the environment provided by the other six oxygen atoms. The $K^+ \cdots O$ distances are listed in Table 4.2.10 along with the 28 $O \cdots K^+ \cdots O$ angles.

TABLES AND DIAGRAMS

Table 4.2.1

Fractional coordinates ($\underline{x}$, $\underline{y}$, $\underline{z}$) and absolute orthogonal coordinates (in Å with $X' = \underline{a}\underline{x}\sin\beta$, $\underline{Y} = \underline{b}\underline{y}$, $\underline{Z}' = \underline{a}\underline{x}\cos\beta + \underline{c}\underline{z}$, and with standard deviations in parentheses).

	$\underline{x}$	$\underline{y}$	$\underline{z}$	$\underline{X}'$	$\underline{Y}$	$\underline{Z}'$
K^+	0.2696	0.0047	0.6076	1.889(9)	0.087(9)	4.802(9)
O(1)	-0.0790	0.0813	0.0640	-0.554(6)	1.498(7)	0.772(6)
O(2)	0.0391	0.0442	0.3126	0.274(6)	0.815(9)	2.718(7)
O(3)	0.4650	0.1209	-0.1248	3.258(6)	2.229(9)	-2.287(7)
O(4)	0.6083	0.0750	0.1123	4.263(6)	1.323(7)	-0.499(6)
O(5)	-0.3209	0.1740	-0.2709	-2.248(8)	3.207(7)	-1.643(7)
O(6)	-0.4503	0.0887	-0.4507	-3.156(7)	1.634(6)	-2.941(6)
O(7)	0.1977	0.2120	-0.2836	1.385(8)	3.908(9)	-3.045(9)
O(8)	0.0225	0.1157	-0.3843	0.158(8)	2.133(7)	-3.517(10)
C(1)	0.0628	0.0626	0.1912	0.440(5)	1.155(5)	1.566(5)
C(2)	0.2547	0.0632	0.1722	1.785(5)	1.165(5)	0.919(5)
C(3)	0.2653	0.1022	0.0276	1.859(5)	1.884(6)	-0.410(6)
C(4)	0.4574	0.0987	0.0073	3.205(4)	1.819(5)	-1.070(5)
C(5)	-0.3664	0.1466	-0.4131	-2.568(5)	2.702(5)	-2.811(5)
C(6)	-0.3051	0.1927	-0.5241	-2.138(5)	3.552(6)	-3.963(5)
C(7)	-0.1172	0.2328	-0.4480	-0.821(5)	4.292(5)	-3.743(6)
C(8)	0.0401	0.1805	-0.3702	0.281(6)	3.328(6)	-3.433(6)
H(1)	-0.2047	0.0798	0.0840	-1.434(9)	1.471(11)	1.264(10)
H(2)	-0.3841	0.1466	-0.2073	-2.691(12)	2.702(12)	-0.913(12)

Table 4.2.1 (cont'd)

	x	y	z	x'	y	z'
H(3)	0.2931	0.1743	-0.2297	2.054(12)	3.213(15)	-2.797(13)
H(4)	0.2997	0.0063	0.1705	2.086(15)	0.115(15)	0.796(18)
H(5)	0.3549	0.0854	0.2799	2.486(12)	1.572(20)	1.641(11)
H(6)	0.1647	0.0807	-0.0725	1.154(12)	1.488(21)	-1.062(12)
H(7)	0.2349	0.1603	0.0349	1.646(17)	2.955(15)	-0.269(19)
H(8)	-0.4191	0.2314	-0.5777	-2.937(13)	4.266(15)	-4.162(14)
H(9)	-0.3031	0.1589	-0.6233	-2.124(18)	2.924(17)	-4.861(13)
H(10)	-0.0818	0.2646	-0.5346	-0.573(16)	4.878(17)	-4.612(17)
H(11)	-0.1311	0.2714	-0.3555	-0.918(16)	5.004(13)	-2.876(17)

Table 4.2.2

Vibrational parameters ($\mathring{A}^2 \times 10^4$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K^+	168(37)	252(44)	119(40)	98(32)	67(34)	106(32)
O(1)	134(25)	566(38)	238(29)	46(24)	121(24)	138(27)
O(2)	156(28)	910(57)	267(32)	-42(30)	104(26)	221(35)
O(3)	168(26)	799(50)	335(34)	50(28)	167(27)	264(34)
O(4)	106(23)	507(37)	247(29)	73(22)	62(23)	67(26)
O(5)	464(37)	339(31)	354(33)	-216(27)	261(30)	-121(27)
O(6)	385(32)	319(30)	221(29)	-144(27)	1107(26)	-53(26)
O(7)	308(35)	578(49)	533(45)	-81(33)	-40(34)	162(39)
O(8)	371(36)	342(36)	750(56)	132(28)	148(38)	-34(36)
C(1)	104(19)	369(25)	179(22)	-29(18)	89(19)	9(20)
C(2)	92(20)	410(27)	213(24)	6(19)	77(19)	105(21)
C(3)	145(21)	446(29)	292(26)	92(20)	123(21)	181(23)
C(4)	107(19)	316(24)	282(25)	20(18)	120(19)	54(21)
C(5)	190(21)	277(23)	159(22)	-40(18)	65(19)	-43(19)
C(6)	260(26)	352(27)	238(26)	-58(21)	57(23)	78(21)
C(7)	218(24)	265(25)	377(28)	-20(19)	71(23)	130(22)
C(8)	274(26)	387(29)	301(28)	17(21)	124(24)	93(24)
H(1)	217(43)	489(56)	259(45)	66(38)	92(40)	47(42)
H(2)	391(53)	567(66)	446(60)	-197(50)	214(48)	-60(54)
H(3)	303(54)	807(87)	459(64)	100(54)	89(51)	273(64)

Table 4.2.2 (cont'd)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
H(4)	589(78)	650(85)	978(110)	249(66)	497(83)	436(81)
H(5)	234(51)	1528(142)	136(47)	-256(70)	5(43)	-17(66)
H(6)	277(51)	1699(167)	218(56)	-194(78)	82(46)	186(76)
H(7)	807(97)	571(77)	1082(112)	365(73)	714(95)	387(79)
H(8)	394(63)	659(82)	597(75)	113(58)	43(57)	329(68)
H(9)	849(102)	808(96)	391(68)	-207(82)	331(71)	-5(64)
H(10)	567(80)	822(102)	767(90)	-188(71)	199(72)	472(84)
H(11)	679(85)	412(66)	771(90)	3(62)	214(74)	-104(66)

Table 4.2.3

Observed structure amplitudes and final calculated structure factors. (×10)

0,2,L

7	84	-99

0,5,L

5	78	-90

0,6,L

0	68	-78

0,7,L

4	84	99
6	80	92

1,3,L

-7	89	104
-6	90	-101

1,10,L

4	83	-100
5	75	84
6	66	-72

6,2,L

1	110	131

4,4,L

3	95	110

0,0,L

2	59	59
4	20	-9
6	41	39

0,1,L

4	27	-26
5	38	44
6	56	-59
7	47	47
8	41	43

0,2,L

0	42	54
1	29	29
3	49	50
4	34	-34
6	41	37
8	21	-20

0,3,L

1	52	59
2	63	-71
5	37	35
6	34	-34
7	34	-34
8	19	-18

0,4,L

2	66	-71
3	43	-42
4	32	35
5	37	38
8	26	-24

0,5,L

2	20	-15
3	26	19
4	39	-39
6	47	-46
7	34	-29
8	41	-38

0,6,L

1	35	-31
2	30	-25
3	31	-32
4	34	-34
5	43	39
6	66	-68
8	28	29

0,7,L

1	32	-28
3	57	55
7	21	19
8	36	44

0,8,L

0	68	-74
1	27	-26
2	53	52
3	55	51
4	32	-21
6	66	-74
7	19	-19

0,9,L

2	42	38
3	53	56
4	55	-54
6	20	21

0,10,L

0	72	73
1	57	56
3	46	41
4	53	52
6	26	24

0,11,L

2	62	62
3	45	42
4	19	-12
5	37	32

0,12,L

1	47	44
2	34	33
3	50	-53
5	77	-80
6	23	-17

0,13,L

1	20	-22
3	35	-36
4	52	-51

0,14,L

0	23	-21
1	48	45
2	19	-19
3	27	23
4	21	-21
5	28	27

0,15,L

3	44	-46
4	30	-34

0,16,L

0	40	40
1	21	-23
2	36	-35
3	18	-19
4	52	-53

0,17,L

2	25	-17
4	26	29

0,18,L

2	39	-37

0,19,L

1	33	31
3	18	17
4	28	27

0,20,L

2	33	36
3	21	-15

0,21,L

1	30	-30
3	20	17

1,0,L

-10	18	14
-8	34	-35
-6	38	35
-4	56	-61
-2	25	22
4	26	25
6	29	-29
8	76	-76

1,1,L

-9	62	-66
-8	17	20
-7	29	-22
-6	59	-61
-5	38	34
-4	54	59
-3	32	32
-2	51	55
-1	16	-15
1	52	-53
3	21	17
4	29	27
6	37	-29
7	79	-86
8	32	-30

1,2,L

-9	42	-42
-8	51	-49
-7	38	34
-6	38	38
-5	25	-22
-4	55	54
-1	25	-23
1	63	-71
2	67	-70
3	27	-23
5	80	-84
6	20	23

1,3,L

-10	27	-32
-9	17	13
-5	43	-38
-4	44	-46
-3	40	-36
-2	19	-19
0	27	-23
1	57	63
2	27	-22
6	25	-27
8	24	19

1,4,L

-8	44	-43
-7	49	56
-6	45	-47
-5	20	-23
-3	42	36
-2	60	61
-1	59	63
0	54	56
1	60	-66
2	23	22
3	50	48
4	33	28
5	45	-44
6	43	34
7	65	-64
8	31	26

1,5,L

-10	24	-33
-9	39	43
-6	51	51
-5	18	-10
-3	42	-39
0	56	-59
1	24	22
2	45	44
3	44	45
4	35	-31
5	22	23
6	66	-65
7	75	78

1,6,L

-8	65	67
-5	17	-16
-4	36	33
-3	58	-52
-2	17	-12
0	23	22
2	56	57
3	30	28
4	59	-60
6	49	53
7	57	-58

1,7,L

-10	18	19
-9	47	45
-8	50	48
-7	38	-40
-5	26	21
-4	67	66
-3	34	-31
0	54	51
1	48	46
2	39	42
4	56	55
5	42	-40
7	42	36

1,8,L

-9	17	-6
-7	32	29
-6	64	-66
-4	40	39
-3	43	39
-1	68	70
0	39	-34
1	32	31
2	62	63
3	43	38
5	46	47
7	46	45

1,9,L

-9	23	20
-7	35	43
-3	40	39
2	19	12
3	56	-55
4	33	-30
5	53	-52

1,10,L

-7	56	-58
-2	35	28
-1	33	-28
0	46	-44
2	55	-56
3	30	-34

1,11,L

-9	28	-27
-8	25	-30
-7	48	-41
-5	35	31
-3	47	-44
0	33	-29
1	43	43
2	47	-49
3	69	73
5	23	-23
6	74	82

1,12,L

-7	31	-28
-6	27	-29
-4	20	-20
-3	82	-69
-2	19	-21
-1	25	-19
0	21	-25
2	24	18
3	40	-41
5	22	-26
6	19	17

1,13,L

-8	40	-37
-6	42	-43
-4	26	26
-2	62	-60
-1	30	28
0	38	39
2	71	-76
3	57	-58
4	20	5
5	20	-13

1,14,L

-8	37	-37
-6	30	32
-5	24	29
-4	21	23
3	39	-38
5	31	-25

1,15,L

-6	35	33
-4	36	-41
-2	35	-39
-1	28	23
1	66	74
2	74	79
3	24	27

1,16,L

-7	19	5
-6	29	30
-5	25	30
-3	42	40
-2	50	50
0	42	39
3	41	-42

1,17,L

-6	29	28
-5	56	55
-3	45	-44
-2	42	39
-1	29	-28
0	32	24
1	73	-81
2	20	10
3	29	35
5	40	37

1,18,L

-5	20	-15
-3	17	-22
-2	35	33
0	30	35
1	18	13
3	50	52
4	19	-10

1,19,L

-5	24	-25
-4	27	31
-2	19	20
0	22	-21
2	42	-43
3	19	-21

1,20,L

-3	18	3
-2	33	-36
-1	31	31
0	35	-28
2	35	-36
3	28	30

1,21,L

0	25	-26

1,22,L

-1	30	-28

2,0,L

-10	27	-1
-8	62	-65
-6	72	-76
2	76	-85
4	42	-38
6	43	42

2,1,L

-9	19	19
-5	57	-57
-4	62	61
-2	65	67
-1	60	61
0	59	-57
2	31	29
3	42	37
4	57	-57
6	21	12

2,2,L

-9	45	-47
-7	54	-53
-6	27	21
-5	37	35
-4	79	86
-3	38	-31
-1	63	64
0	59	61
1	75	81
3	65	66
6	24	-20

2,3,L

-10	23	-26
-9	24	-21
-6	39	40
-5	66	-65
-4	50	49
-1	61	62
0	19	-17
1	58	-59
2	33	24
3	33	-29
4	19	8
5	54	-55
6	21	20
7	48	48

2,4,L

-9	56	-57
-8	25	-21
-6	31	26
-3	58	55
-2	80	-90
-1	21	19
0	78	-91
3	33	25
4	69	72
6	22	22

2,5,L

-10	19	-12
-9	21	9
-8	37	-37
-7	29	30
-6	54	-51
-5	68	62
-4	43	39
-3	53	48
-2	57	55
1	62	66
2	49	52
3	37	-33
4	40	-34
6	53	-54
7	61	-64

2,6,L

-9	22	-19
-6	65	63
-5	32	25
-2	20	-17
-1	19	-19
0	31	-29
1	83	-95
2	38	-37
4	19	-19
5	22	22

2,7,L

-8	38	41
-7	48	48
-6	20	-19
-4	19	-16
-3	61	-55
-2	30	-26
-1	30	-30
0	70	-76
1	33	27
3	28	25
4	40	-38

2,8,L

-10	22	-12
-9	22	21
-8	41	36

Table 4.2.3 (cont'd)

2,8,L

-6	37	34
-5	18	-18
-4	21	10
-2	25	-24
-1	40	38
3	44	-46
5	40	-42
6	30	34

2,9,L

-9	33	34
-7	21	21
-6	25	22
-4	28	-27
-3	38	-40
-2	63	-62
0	48	48
2	31	24
3	63	-69
4	45	47

2,10,L

-9	41	43
-8	32	26
-7	41	41
-5	26	-23
-4	30	-30
-3	66	-70
-1	42	-42
1	39	-35
2	19	17

2,11,L

-8	21	23
-7	33	-36
-6	37	-33
-4	40	-41
-2	21	-16
0	25	16
1	41	41
5	22	23

2,12,L

-9	30	-32
-3	24	-21
-2	35	41
-1	32	30
0	31	30
1	76	79
2	19	16
3	44	42
5	38	36

2,13,L

-7	21	-23
-5	61	-61
-3	33	-37
-2	60	57
-1	53	49
0	22	17
5	19	-12

2,14,L

-8	45	-47
-7	42	-40
-4	38	36
-3	30	33
-2	59	57
0	29	-25
1	50	-51
2	22	-16
3	20	-15

2,15,L

-6	41	45
-5	18	-8
-4	24	23
-1	55	51
1	18	15

2,16,L

-7	45	-48
-4	42	-46
-3	51	54
-2	38	-37
-1	59	57
1	22	14
2	31	-33

2,17,L

-3	42	40
-2	24	-11
-1	18	-3
0	28	-30
1	23	-19
2	33	-31
3	33	-32

2,18,L

-6	28	29
-4	26	-28
-1	62	-62
1	29	-27

2,19,L

-3	21	-19
-2	37	36
2	33	33

2,20,L

-4	27	33
-2	20	-22
3	18	10

2,21,L

-2	29	-30

3,0,L

-10	35	37
-8	18	-17
-6	80	-84
-2	75	-81
0	53	53
4	29	29
6	36	35

3,1,L

-9	62	-59
-8	84	-88
-6	88	-95
-4	44	-39
-2	75	81
-1	41	-39
0	23	-19
2	45	-37
3	50	44
6	17	18

3,2,L

-10	23	17
-9	24	-17
-8	42	-42
-7	69	72
-6	33	31
-5	33	-29
-3	17	-18
-2	53	-47
1	17	15
4	22	-11
5	32	-32
6	59	-63

3,3,L

-9	39	39
-8	37	-36
-7	33	-32
-6	44	-39
-5	54	-52
-4	23	-21
-3	25	-20
-2	89	103
-1	78	83
0	69	69
2	21	17
4	32	-36
5	17	13
6	32	-33

3,4,L

-9	36	-35
-8	33	33
-7	46	-43
-6	36	37
-5	56	-53
-1	67	66
0	21	-18
1	23	20
2	19	-17
3	49	-41
4	22	14
6	36	36

3,5,L

-10	36	-37
-8	53	51
-7	40	39
-6	20	-23
-4	21	-13
-3	63	59
-2	56	-53
-1	32	28
0	55	56
1	74	-77
2	64	64
3	56	-56
5	27	-23

3,6,L

-8	66	70
-7	41	45
-2	88	102
0	37	31
2	45	-40
3	25	-24
5	36	-35
6	18	-14

3,7,L

-10	17	16
-8	24	21
-7	38	37
-6	27	23
-5	19	17
-4	24	-22
-3	85	95
-1	59	-58
0	57	-55
1	52	-50
4	35	-36
5	44	42

3,8,L

-10	22	-19
-9	21	-21
-8	25	21
-7	34	37
-6	26	-23
-5	27	30
-4	31	-26
-3	39	-39
-1	56	-54
0	64	-63
3	43	42
5	55	56

3,9,L

-8	45	46
-7	72	-74
-6	23	21
-4	45	42
-1	38	37
0	54	-51
1	36	-36
2	23	-10
4	35	-36

3,10,L

-7	38	-39
-6	24	-26
-5	27	27
-4	31	-32
-1	24	-21
0	26	-19
1	71	-73
3	29	27
5	29	23

3,11,L

-7	21	-27
-6	32	-31
-5	44	-47
-4	58	59
-2	39	-41
-1	48	-45
0	34	-28
4	32	29

3,12,L

-8	24	24
-7	21	-17
-6	37	-36
-5	28	33
-4	67	-66
-3	32	31
-2	46	-47
1	65	67
4	32	35

3,13,L

-8	25	-24
-4	29	-26
-3	31	30
-2	19	12
-1	64	64
1	44	47
2	19	10
3	39	-42
4	17	20

3,14,L

-7	18	-20
-6	22	23
-4	27	-28
-1	51	-52
0	18	-7
1	25	-28
2	65	72
3	31	-32

3,15,L

-6	25	-25
-5	17	18
-3	37	-39
-1	27	-22
0	70	70
1	21	-22
2	26	25
4	40	-42

3,16,L

-6	32	36
-4	18	18
-3	22	10
-1	24	22
0	39	38
3	21	25
4	25	21

3,17,L

-5	22	15
-3	22	23
0	21	20
3	17	20

3,18,L

-4	19	9
1	23	29
2	34	-37

3,19,L

-2	22	22
0	24	-19
1	23	-22

3,20,L

0	21	-10

4,0,L

-8	59	54
-6	54	50
-4	17	1
0	80	86
2	60	-56

4,1,L

-10	24	23
-9	36	-34
-8	54	50
-6	59	-61
-4	17	15
-3	47	-46
-2	38	-36
-1	36	35
0	44	44
1	21	-22
3	76	81
4	66	64
5	66	67

4,2,L

-10	17	19
-8	43	-45
-7	80	79
-5	28	-24
-3	44	-40
-1	40	39
0	46	42
1	40	35
3	33	29
4	46	39
5	57	-55

4,3,L

-10	20	-7
-9	21	-22
-8	95	107
-7	69	71
-6	34	32
-4	23	21
-3	41	36
-2	23	23
-1	61	-58
0	56	-52
2	40	39
3	31	-25
4	23	-20
5	28	32

4,4,L

-7	29	27
-6	43	-43
-3	20	20
-2	49	-45
-1	63	63
0	33	-30
1	33	30
4	56	-58
5	53	52

4,5,L

-10	35	-41
-9	41	-45
-8	25	23
-7	40	-37
-6	20	-19
-5	45	45
-4	54	-53
-3	32	-30
-2	51	46
-1	19	-12
0	43	-41
1	43	-37
2	35	35
3	18	18
4	21	19
5	69	-73

4,6,L

-9	29	-27
-8	21	20
-6	46	-41
-5	44	-42
-4	18	19
-3	26	-13
0	49	-43
1	78	-81
4	67	-73

4,7,L

-10	40	-39
-9	47	50
-8	23	-24
-7	52	-53
-6	55	-57
-5	24	24
-4	47	51
-3	48	48
-1	25	-20
1	18	16
3	61	-65
4	50	47
5	68	-76

4,8,L

-9	20	-14
-7	34	-36
-6	50	-52
-4	19	16
-3	27	-29
0	18	10
2	27	25
3	54	-53
4	29	-24

4,9,L

-9	23	24
-6	37	-36
-5	26	21
-4	54	-54
-3	64	68
-2	41	-41
-1	18	-18
0	29	-28
1	71	76
3	26	29
4	37	-37

4,10,L

-9	33	27
-8	49	50
-6	40	-33
-5	52	52
-4	40	36
-2	80	87
-1	22	-23
0	58	58
2	53	50
3	73	-79
4	23	-17

4,11,L

-6	61	61
-5	44	41
-4	54	57
-3	18	-14
-2	41	41
-1	82	-92
0	42	41
1	17	-15
2	40	-38
3	66	69

4,12,L

-6	22	22
-5	29	34
-3	69	-68
0	29	-29
1	63	67

4,13,L

-7	18	-22
-6	19	12
-4	52	54
-3	31	-27
-1	22	15
0	24	23
2	36	-31

4,14,L

-8	32	-36
-6	25	20
-5	34	35
-3	32	31
-2	59	-62
-1	31	34
0	42	-39
1	32	29

4,15,L

-5	19	-18
-4	38	-39
-3	23	-23
-2	52	-49
-1	21	-27
1	31	-31
2	19	17
3	38	-39

4,16,L

-7	51	-57
-4	52	-52
-2	40	35
-1	18	-13
0	17	16

Table 4.2.3 (cont'd)

4,16,L

2	37	-36
3	18	22

4,17,L

-6	20	4
-5	47	49
-4	23	-18
1	22	-20
2	27	31

4,18,L

-4	29	-37
-3	44	-39
0	32	35

4,19,L

-3	26	23
-1	22	23

5,0,L

-10	19	20
-8	44	38
-4	89	-98
0	41	-39
2	92	-97
4	19	-21

5,1,L

-10	18	-15
-8	34	-30
-7	111	129
-6	48	-46
-3	73	-70
0	98	-110
1	63	-64
2	39	-37
3	58	59

5,2,L

-9	23	28
-8	27	20
-7	78	-82
-3	71	-66
-2	25	19
-1	37	-36
1	18	-14
2	24	27
4	28	20

5,3,L

-10	37	-37
-8	28	-26
-6	102	-111
-5	65	-67
-4	19	12
-2	36	35
-1	76	73
0	89	-94
1	44	-41
2	33	30
3	48	-46

5,4,L

-9	20	22
-7	24	-25
-6	17	13
-5	46	-41
-4	53	51
-2	27	-27
-1	77	-79
1	81	-87
4	20	23

5,5,L

-10	20	15
-9	38	-37
-8	48	50
-7	53	-49
-6	87	-88
-4	59	-56
-3	37	32
-1	43	44
0	32	-30
1	94	109
2	56	60
3	29	28

5,6,L

-8	76	-90
-7	17	20
-6	36	-38
-4	27	28
-3	57	59
-2	66	63
0	38	32
1	49	44

5,7,L

-8	61	67
-7	38	-40
-6	42	42
-5	36	37
-4	78	84
-3	45	-40
-2	65	65
-1	80	-84
1	31	32
2	60	57

5,8,L

-8	28	-34
-6	35	29
-5	51	52
-4	87	94
-3	18	15
-1	85	91
1	31	28
3	40	34

5,9,L

0	19	7
1	54	56
2	22	-23
3	18	-13

5,10,L

-9	32	-32
-7	20	20
-5	39	35
-2	65	-68
-1	27	23
1	19	13
2	24	-28
3	24	-22

5,11,L

-8	34	-37
-7	18	6
-5	61	61
-4	29	-25
-2	22	-20
-1	41	-36
0	18	-4
2	48	-46
3	47	-49

5,12,L

-4	45	-50
-3	81	-92
-1	41	-43
0	22	-23
1	32	-32
3	40	-42

5,13,L

-8	23	-28
-5	51	-52
-4	46	-52
-3	50	-53
-2	38	-37
-1	24	21

5,14,L

-8	20	-21
-3	37	-40
-2	17	18
-1	20	17
1	30	-25
3	22	-27

5,15,L

-6	33	30
-4	38	-41
-3	18	-15
0	44	44
1	20	-16

5,16,L

-6	24	12
-4	20	-29
-3	22	20
-2	42	43

5,17,L

-3	51	-53
-2	36	-37

5,19,L

-7	19	-9

5,14,L

2	35	-32

5,17,L

-5	16	-10
-4	36	37
-2	33	33
1	34	32

5,18,L

-3	37	42
-2	19	26
-1	30	34

6,0,L

-8	36	40
-6	47	-47
-2	18	20
0	67	-65
2	28	-28

6,1,L

-10	32	32
-9	32	-28
-7	21	22
-5	58	-55
-4	52	-50
-3	27	26
-1	53	-55
0	41	-42
1	70	-69
2	49	49

6,2,L

-9	19	19
-8	28	25
-7	69	77
-5	24	24
-3	20	20
-2	26	-22
0	92	-100

6,3,L

-9	29	33
-8	53	48
-5	27	-25
-4	54	54
-1	74	74
0	52	50
1	48	-45
2	75	76

6,4,L

-8	18	-6
-7	42	-43
-6	62	60
-4	57	54
-3	19	-21
-2	17	12

6,5,L

-3	27	24
-2	87	-92
-1	44	40
0	37	-36
1	63	64
2	36	37

6,6,L

-7	44	-42
-6	58	-59
-5	33	32
-2	19	-8
0	84	90
1	23	19

6,7,L

-8	40	-38
-7	34	-34
-6	35	-35
-2	24	20
-1	76	75
0	68	-68
1	34	33

6,8,L

-4	30	-33
-3	20	-18
-1	63	-64
0	51	48
1	75	-75
3	31	-33

6,9,L

-8	18	19
-7	66	-70
-5	31	-25
-3	56	-59
-2	42	40
0	26	25
3	20	-19

6,10,L

-8	19	-16
-7	26	-23
-6	21	21
-4	36	-36
-3	22	-18
-1	41	44
1	19	-23
2	46	-45

6,11,L

-6	17	15
-4	17	-10
-3	42	-38
-2	35	38
-1	34	-36
2	29	-30

6,12,L

-7	29	31
-6	34	40
-4	23	19
-2	20	-22
-1	62	67
0	42	-42
1	26	26
2	16	-21

6,13,L

-6	45	51
-3	25	33
-2	25	16
2	19	-16

6,14,L

-6	54	60
-3	27	35
0	43	-43

6,15,L

-4	36	-37
-3	48	50
-1	23	18
0	32	34

6,16,L

-2	46	48
-1	32	-40

7,0,L

-8	25	29
-4	66	99
-2	72	73
2	18	20

7,1,L

-5	23	22
-4	71	72
-3	23	21
-2	27	-23
0	35	-36
1	19	-19

7,2,L

-9	23	-23
-7	31	-30
-6	55	-60
-5	29	28
-3	25	-27
-2	54	-53
0	18	13
1	27	-22
2	27	25

7,3,L

-8	19	-20
-6	20	-27
-4	48	45
-3	71	70
0	25	-23
1	47	-45

7,4,L

-8	23	21
-7	40	-39
-6	25	-24
-5	36	32
-1	51	-48
2	25	20

7,5,L

-8	17	10
-7	51	-56
-6	19	-15
-5	31	-25
-3	49	-49
-2	27	32

7,6,L

-8	28	28
-5	19	7
-3	50	-55
-2	17	-19
0	25	-28

7,7,L

-6	20	-18
-5	21	15
-3	28	-27
-1	20	22
0	25	22
1	20	20
2	26	24

7,8,L

-6	40	39
-5	20	12
-4	20	-17
-3	27	19
-2	34	-35
-1	24	25
1	27	26

7,9,L

-6	31	29
-5	28	27
-4	35	-33
-3	19	19
-1	37	-37
1	22	27

7,10,L

-7	21	-25
-5	27	23
-4	34	-36
-2	22	23
-1	18	15
0	37	36

7,11,L

-5	40	47
-3	29	32
-2	42	44
1	36	-40

7,12,L

-6	20	-19
-3	34	-31
-1	23	-18
0	17	14

7,13,L

-5	29	-27
-3	39	40
-1	23	17

8,0,L

-6	27	-30
-2	65	72

8,1,L

-7	55	55
-6	21	12
-5	36	33
-4	33	34
-3	30	-32
-2	21	13
-1	18	10

8,2,L

-5	54	-54
-3	52	-51
-2	30	-29
-1	49	53
1	41	44

8,3,L

-6	40	-39
-4	54	-60
-2	33	37

8,4,L

-7	19	23
-3	31	34
-2	25	-23
1	25	29

8,5,L

-6	27	-29
-5	25	28
-4	37	-31
-3	27	-23
-1	17	-13

8,6,L

-6	41	-46

8,7,L

-6	20	-23
-4	19	20
-3	19	17
-1	36	-37
0	19	-13

8,8,L

-4	34	31
-3	30	-31
-2	45	49
-1	26	-22

8,9,L

-5	19	13

Table 4.2.4

Analysis of structure-amplitude agreement. ($\underline{N}$ is the number of reflections in each group.)

(a) As a function of $(\sin\theta)/\lambda$

Range	ΣF_o	$\Sigma\Delta$	$\underline{N}$	$\underline{R}$	$(\Sigma\Delta)/\underline{N}$
0.0 - 0.1	13.64	1.76	5	0.129	0.352
0.1 - 0.2	203.44	16.15	42	0.079	0.384
0.2 - 0.3	614.40	47.62	136	0.078	0.350
0.3 - 0.4	1057.04	85.26	247	0.081	0.345
0.4 - 0.5	1706.77	130.50	407	0.076	0.320
0.5 - 0.6	1077.05	122.06	359	0.113	0.340
0.6 - 0.7	28.29	3.62	10	0.128	0.362

(b) As a function of $\underline{F_o}$

0.0 - 3.0	1066.16	177.96	470	0.167	0.379
3.0 - 5.0	1684.95	116.59	435	0.069	0.278
5.0 - 7.0	1269.99	54.06	217	0.043	0.249
7.0 - 9.0	590.48	47.05	75	0.080	0.626
9.0 -11.0	89.06	11.32	9	0.127	1.255
ALL	4700.64	406.98	1206	0.086	0.337

Table 4.2.5

Low-order reflections affected by extinction which were removed from the final stages of refinement.

h	k	l
0	1	2
0	4	0
0	4	1
0	5	1
1	0	2
1	0	-2
1	9	-1
2	0	0
2	0	-2
2	0	-4
3	0	-4

Table 4.2.6

Interatomic distances (Å) and angles (degrees) within the succinate residues (standard deviations in parentheses).

C(1)-O(1)	1.317(6)	C(5)-O(5)	1.312(8)
C(1)-O(2)	1.212(9)	C(5)-O(6)	1.226(8)
C(1)-C(2)	1.493(7)	C(5)-C(6)	1.495(8)
C(2)-H(4)	1.099(16)	C(6)-H(8)	1.090(14)
C(2)-H(5)	1.087(12)	C(6)-H(9)	1.093(16)
C(2)-C(3)	1.513(8)	C(6)-C(7)	1.526(7)
C(3)-H(6)	1.038(13)	C(7)-H(10)	1.077(19)
C(3)-H(7)	1.101(16)	C(7)-H(11)	1.126(17)
C(3)-C(4)	1.501(7)	C(7)-C(8)	1.497(7)
C(4)-O(3)	1.277(9)	C(8)-O(7)	1.306(9)
C(4)-O(4)	1.233(6)	C(8)-O(8)	1.204(9)
O(1)-C(1)-O(2)	122.9(0.6)	O(5)-C(5)-O(6)	123.1(0.6)
O(1)-C(1)-C(2)	114.6(0.5)	O(5)-C(5)-C(6)	113.4(0.5)
O(2)-C(1)-C(2)	122.5(0.4)	O(6)-C(5)-C(6)	123.5(0.5)
C(1)-C(2)-C(3)	115.4(0.4)	C(5)-C(6)-C(7)	114.4(0.4)
H(4)-C(2)-H(5)	104.9(1.3)	H(8)-C(6)-H(9)	103.4(1.1)
C(2)-C(3)-C(4)	114.2(0.4)	C(6)-C(7)-C(8)	110.7(0.4)
H(6)-C(3)-H(7)	108.7(1.4)	H(10)-C(7)-H(11)	107.3(1.3)
C(3)-C(4)-O(3)	116.1(0.4)	C(7)-C(8)-O(7)	113.5(0.5)
C(3)-C(4)-O(4)	121.4(0.6)	C(7)-C(8)-O(8)	123.3(0.5)
O(3)-C(4)-O(4)	122.5(0.6)	O(7)-C(8)-O(8)	123.2(0.7)

Table 4.2.7

Sums of, and differences between, C — O distances, and differences between C — C — O angles in the carboxyl groups.

Unit	R_1		R_2	
Carboxyl group	C(5)	C(8)	C(4)	C(1)
Σ(C — O),(Å)	2.528	2.510	2.510	2.529
Δ(C — O),(Å)	0.044	0.105	0.086	0.102
Δ(C — C — O), (deg.)	10.1	9.8	5.3	7.9

Table 4.2.8

Torsion angles* (degrees) in the succinate residues, with standard deviations in parentheses.

Atom A	Atom B	Atom C	Atom D	Angle
O(1)	C(1)	C(2)	C(3)	14.7(0.5)
O(2)	C(2)	C(2)	C(3)	-167.6(0.4)
C(1)	C(2)	C(3)	C(4)	-177.1(0.3)
C(2)	C(3)	C(4)	C(3)	169.6(0.4)
C(2)	C(3)	C(4)	C(4)	-10.2(0.4)
C(5)	C(5)	C(6)	C(7)	34.5(0.5)
O(6)	C(5)	C(6)	C(7)	-145.1(0.5)
C(5)	C(6)	C(7)	C(8)	57.3(0.4)
C(6)	C(7)	C(8)	O(7)	-170.6(0.3)
C(6)	C(7)	C(8)	O(8)	8.5(0.4)

*The angle A-B-C-D is defined as positive if when viewed along the B-C bond atom A has to be rotated clockwise to eclipse atom D.

Table 4.2.9

Interatomic distances (A) and angles (degrees) in the hydrogen bonds, with standard deviations in parentheses.

O(1) ... O(4)^{I}	2.579(9)	O(1)-H(1) ... O(4)^{I}	178.1(1.0)
O(1)-H(1)	1.009(12)	C(1)-O(1)-H(1)	110.9(0.8)
H(1) ... O(4)^{I}	1.571(12)	C(1)-O(1) ... O(4)^{I}	111.1(0.5)
O(5) ... O(3)^{I}	2.573(11)	O(5)-H(2) ... O(3)^{I}	162.6(1.2)
O(5)-H(2)	0.991(16)	C(5)-O(5)-H(2)	110.5(0.9)
H(2) ... O(3)^{I}	1.610(16)	C(5)-O(5) ... O(3)^{I}	110.6(0.5)
O(7) ... O(3)	2.630(10)	O(7)-H(3) ... O(3)	172.3(1.3)
O(7)-H(3)	0.996(15)	C(8)-O(7)-H(3)	109.4(1.1)
H(3) ... O(3)	1.639(14)	C(8)-O(5) ... O(3)	113.9(0.6)

Table 4.2.10

Environment of the potassium ion: $K^+ \cdots O$ distance ($\mathring{A}$) and $O \cdots K^+ \cdots O$ angles (degrees); standard deviations of angles $\sim 0.4^\circ$.

$K(1) \cdots O(2)$	2.736(9)	$K(1) \cdots O(6^{II})$	2.834(12)
$K(1) \cdots O(2^{III})$	2.775(12)	$K(1) \cdots O(6^{IV})$	2.781(12)
$K(1) \cdots O(3)$	3.189(11)	$K(1) \cdots O(8^{II})$	3.282(11)
$K(1) \cdots O(4^{VI})$	2.797(10)	$K(1) \cdots O(8^{V})$	2.767(12)

	$O(2)$	$O(2^{III})$	$O(3)$	$O(4^{VI})$	$O(6^{II})$	$O(6^{IV})$	$O(8^{II})$	$O(8^{V})$
$O(2)$	0	91.97	122.34	157.72	85.70	86.23	60.88	67.85
$O(2^{III})$		0	103.29	69.05	120.15	165.00	60.24	67.66
$O(3)$			0	75.07	127.78	65.69	163.46	67.80
$O(4^{VI})$				0	93.74	115.14	98.39	112.53
$O(6^{II})$					0	74.60	67.07	153.10
$O(6^{IV})$						0	130.14	98.00
$O(8^{II})$							0	101.96
$O(8^{V})$								0

Table 4.2.11

Subset of reflections used in the initial Σ_2 solution and their F_b- and F_b+ values (as defined in the text). The reflections are listed in order of decreasing E .

h	k	l	F_b-	F_b+	h	k	l	F_b-	F_b+
6	2	1	13.07	14.28	5	1	7	11.67	12.87
4	3	-8	10.33	7.36	5	3	-6	15.89	11.07
6	2	0	-10.05	-5.04	5	6	-8	-9.04	-6.52
5	5	1	5.96	4.72	6	6	0	9.03	7.36
6	8	1	-7.49	-6.04	5	1	0	-11.01	-10.08
5	12	-3	-9.19	-12.90	5	5	-6	-8.76	-8.95
3	1	-8	-8.82	-8.35	4	1	4	9.43	6.96
6	5	-2	-9.42	-2.68	6	3	2	7.65	12.54
5	8	-4	9.35	12.43	6	9	-7	-7.02	-7.96
1	11	6	8.22	9.13	1	1	7	-8.57	-13.03
4	7	5	-7.58	-5.79	5	2	-7	-8.18	-7.76
5	8	-1	9.06	5.85	5	3	0	9.43	6.96
6	7	-1	7.99	5.86	4	5	5	-7.32	-5.68
4	10	3	-7.93	-3.85	1	5	7	7.76	8.90
1	17	1	-8.06	-5.74	0	2	7	-9.88	-7.90
7	1	-4	7.23	3.45	6	2	-7	7.67	1.72
4	2	-7	7.88	9.24	4	11	-1	-9.20	-6.29
7	3	-3	6.98	6.01	0	12	5	-8.02	-9.20

Table 4.2.11 (cont'd)

h	k	l	F_b-	F_b+	h	k	l	F_b-	F_b+
8	1	-7	5.46	7.37	6	14	-6	5.98	5.60
5	4	1	-8.66	-6.12	3	1	-6	-9.54	-9.69
3	9	-7	-7.44	-3.69	6	12	-1	6.67	7.84
1	15	2	7.87	5.28	5	7	-1	-8.45	-7.88
0	7	6	9.20	4.77	4	1	5	6.69	6.04
6	1	1	-6.89	-7.41	4	16	-7	-5.70	-5.30
4	11	3	6.90	3.84	5	7	-4	8.38	5.91
5	7	-8	6.75	7.81	6	7	0	-6.77	-5.70
3	15	0	7.04	7.31	1	1	-9	-6.55	-4.43
1	10	5	8.44	11.68	6	3	-1	7.38	3.09
4	10	-2	8.71	7.12	1	12	-3	-8.92	-4.00
3	6	8	6.99	3.82	2	18	1	-6.21	-3.42
4	6	4	-6.98	-3.32	3	1	-9	-5.90	-8.27
4	1	3	8.07	4.42	1	10	6	-7.23	-5.84
8	2	-5	-5.45	-2.72	3	14	2	7.22	5.82
1	6	-8	6.70	5.11	2	5	7	-6.45	-5.01
1	17	-5	5.54	5.62	8	3	-4	-5.98	-2.87
6	5	1	6.39	4.80	5	4	-1	-7.90	-4.11
4	12	-3	-6.78	-6.95	1	2	5	-8.38	-5.50
3	7	3	9.55	4.73	4	6	1	-8.12	-4.24
4	3	-7	7.11	6.46	1	4	7	-6.43	-8.26
6	8	-1	-6.37	-6.37	3	6	-2	10.15	11.21

Table 4.2.12

Reflections whose phases were incorrectly determined by the symbolic addition procedure, along with their F_o, F_{b-} and F_{b+} values (as defined in the text).

h	k	l	F_o	F_{b-}	F_{b+}
8	2	-5	5.45	-5.45	-2.72
8	3	-4	5.42	-5.98	-2.87
0	8	6	6.65	-7.38	-3.33
8	2	-3	5.15	-5.14	-5.28
5	1	3	5.76	5.94	3.14
1	13	3	5.75	-5.80	-1.37
7	13	-3	3.90	4.04	1.57
3	2	6	5.86	6.30	-0.88
6	6	-6	5.85	5.91	-0.13
4	10	-8	4.89	4.97	4.05
1	13	-2	6.17	-5.98	-4.88

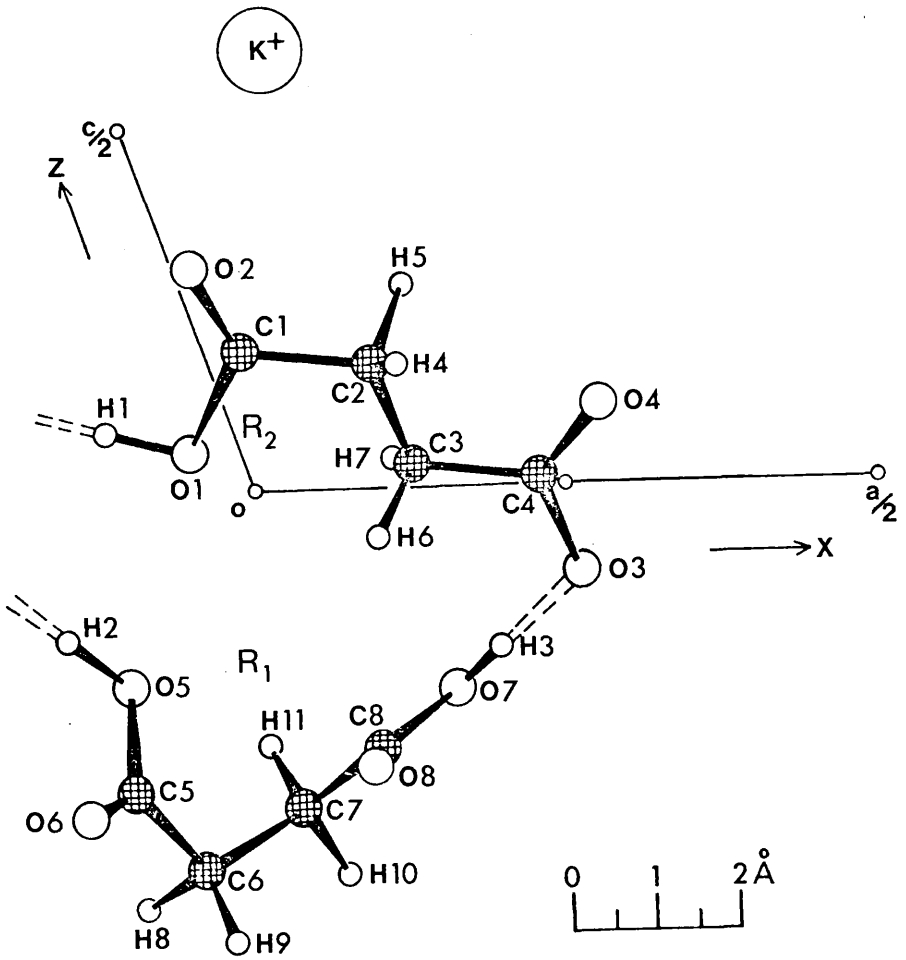


Figure 4.2.1 : KH_3Succ_2 - the crystal-chemical-unit (C.C.U) and numbering scheme.

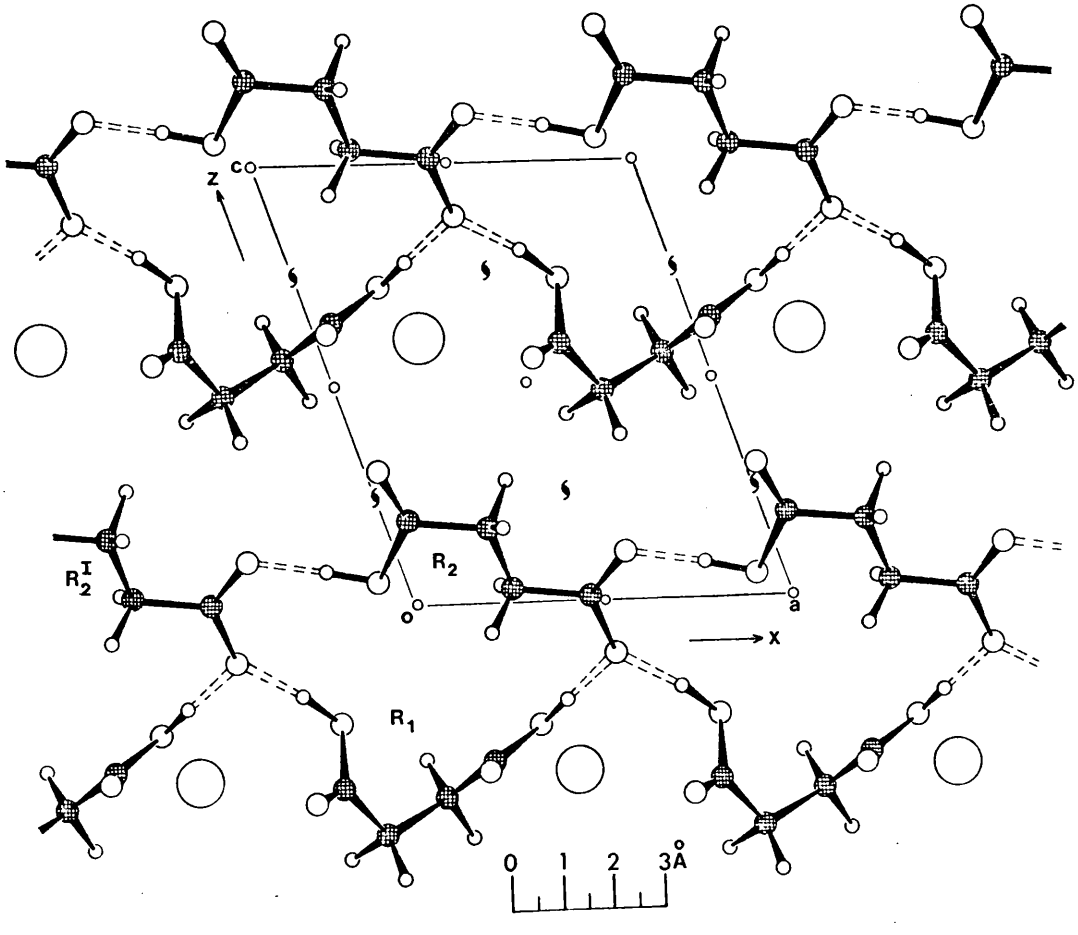


Figure 4.2.2 : The crystal structure of KH_3Succ_2 projected along the b axis from y = 0 to y = $\frac{1}{4}$.

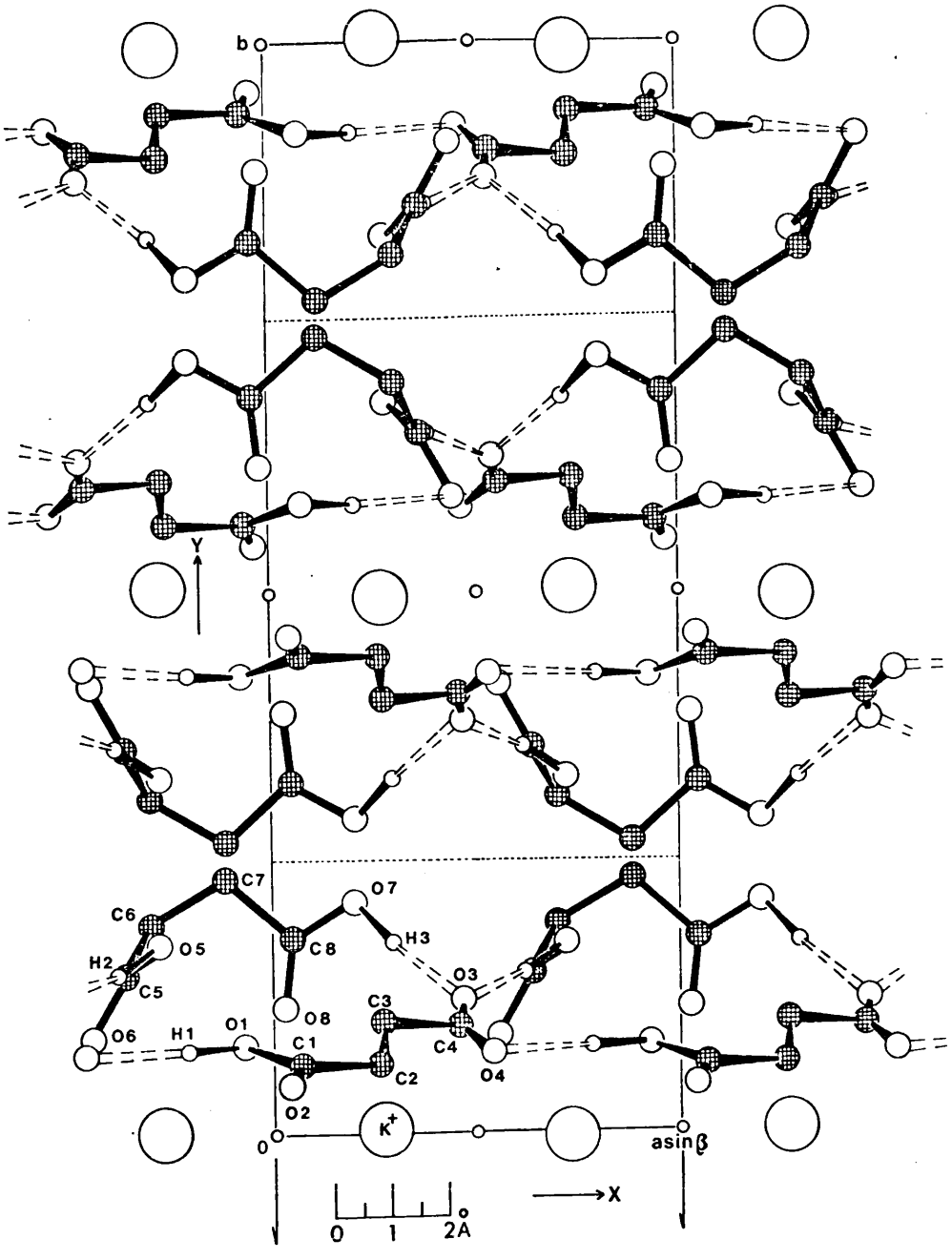


Figure 4.2.3 : The crystal structure of KH_3Succ_2 projected along the c axis.

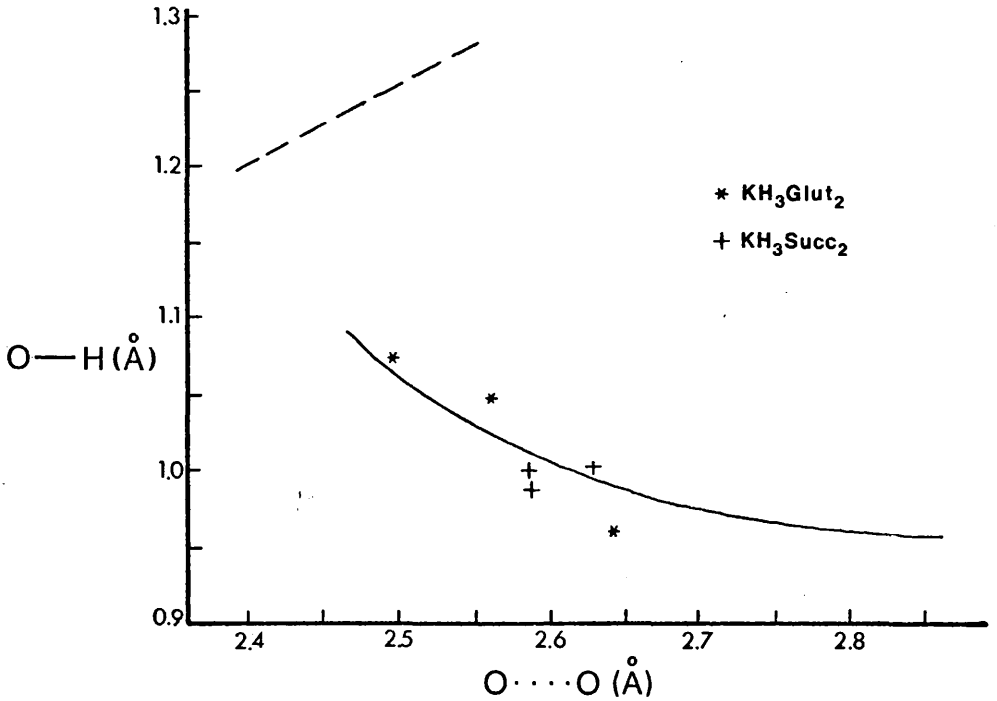


Figure 4.2.4 : Graph showing the Nakamoto-Margoshes-Rundle relationship between O...O and O-H distances in hydrogen bonds. The graph is that given by Hamilton and Ibers[9]. The diagonal broken line corresponds to hypothetical centrosymmetric bonds. The values obtained from the analyses of KH_3Succ_2 and KH_3Glut_2 are indicated by crosses and stars respectively.

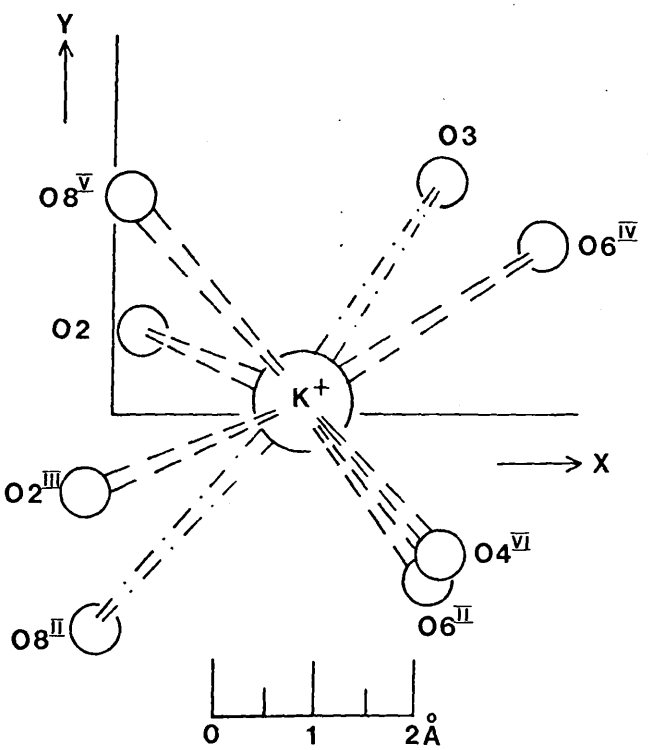


Figure 4.2.5 : The environment of the potassium ion. The two questionable K^+... O contacts are represented by dot-dash lines.

4.3. The Crystal Structure of potassium tri-hydrogen di-glutarate

4.3.1. Introduction

Unlike potassium tri-hydrogen di-succinate, small crystals of potassium tri-hydrogen di-glutarate suitable for x-ray analysis are relatively easily grown, and its structure has been solved from x-ray diffraction data by Dr. A.L. Macdonald.[10] However, the x-ray analysis revealed nothing about the positions of the hydrogen atoms in the structure, and a full set of neutron diffraction data were therefore collected in order to locate the hydrogen atoms accurately, in particular, the three hydroxylic protons involved in hydrogen bonding.

4.3.2. Experimental

Crystal Data

The $a\sin\beta$ and b dimensions of the potassium salt were derived from a least-squares treatment of some high-order reflexions on an hko Weissenberg photograph. The other cell dimensions were obtained from precession and rotation photographs.

$KC_{10}H_{15}O_8$, M = 302.10. Monoclinic, a = 11.182(3), b = 12.727(4), c = 9.423(8) Å, β = 92.75(25)°; U = 1339.5 Å^3, D_m = 1.46, z = 4, D_c = 1.495. Space group $P2_1/c$ (No. 14).

Data Collection

Diffracted neutron intensities were measured on a Ferranti Mk 11 four-circle diffractometer mounted in the Dido reactor at A.E.R.E. Harwell using a neutron beam monochromated to 1.172 Å. A crystal of dimensions 6.0 (parallel to c) x 6.5 x 2.0 $m.m.^3$ mounted along c was used, and integrated intensities were measured for some 2,000 reflections out to $\theta = 45^{\circ}$. Of these, only 1009 with $|F| \geq 3\sigma(|F|)$ were used in the analysis, and absorption corrections were applied to these observed data using a calculated μ(effective) of 1.66 cm^{-1}. The incoherent scattering cross-section of hydrogen was taken as 3 7 x 10^{-24} cms.

4.3.3 Structure analysis and refinement.

The observed structure amplitudes were combined with phases calculated from the set of fractional coordinates determined for the non-hydrogen atoms in the x-ray analysis to compute a map of neutron-scattering density in which all fifteen hydrogen atoms were found in their expected positions. The atomic coordinates thus determined were refined by least-squares analysis using the program CRYLSQ; two cycles of full-matrix isotropic least-squares refinement followed by four cycles of block-diagonal anisotropic least-squares refinement reduced R to 0.87. Unit weights were used throughout, and the relative constancy of $(\Sigma\Delta^2/N)$ when analysed at the end of refinement in terms of F_{obs} and $\sin\theta/\lambda$ indicated that a non-unit weighting scheme was not required. The nuclear scattering-lengths used were 0.350, 0.661, 0.577 and -0.378 x 10^{-12} cm for K, C, O and

H respectively.

The final positional and vibrational parameters are given in Tables 4.3.1 and 4.3.2 respectively. The observed structure amplitudes and calculated structure factors are listed in Table 4.3.3 and an analysis of their agreement is given in Table 4.3.4.

4.3.4 Discussion of the structure.

The crystal-chemical unit (C.C.U.) and atomic numbering system is shown in Figure 4.3.1; other symmetry-related units required to describe the structure are given in Table 4.3.5. The crystal structure is represented in Figures 4.3.2 and 4.3.3 and the principal interatomic distances and angles in the glutarate residues are listed in Tables 4.3.6 and 4.3.7 respectively.

The results of the x-ray analysis suggested that R_2 is the glutaric acid molecule and R_1 the acid anion, the carboxyl group centred on C(1) being the ionised carboxylate. The neutron analysis provides confirmation of the x-ray results by locating the hydroxylic protons and also from the dimensions of the four carboxyl groups; the unionised carboxyls have larger differences in their C-O lengths and C-C-O angles (Table 4.3.8).

The crystal structure is based on infinite chains of B_2 type acid anion residues linked head-to-tail by short asymmetric hydrogen bonds, and in this respect is similar to the crystal structure of potassium trihydrogen disuccinate. In this case, however, the chains form two antiparallel helices which spiral around the two-fold screw axes at $\frac{1}{2}$, $\underline{Y}$, $\frac{1}{4}$

and $\frac{1}{2}$, $\underline{Y}$, $\frac{3}{4}$. The helices of different cells are linked together by hydrogen bonding to the unionised glutaric acid molecules; the O(5) carboxyl oxygen of an R_1 residue is linked via an R_2 residue to the O(2) carboxylate oxygen of the equivalent R_1 residue in the cell (101). There is no hydrogen-bonding between helices in the same cell.

The glutaric acid molecule is in an extended form, and the five glutarate chain atoms C(6), C(7), C(8), C(9) and C(10) appear to be coplanar, their mean plane being represented by the equation $-0.2078X' + 0.9449Y - 0.2529Z' = 2.5891$ Å; the root mean square distance of the atoms from this plane is 0.006 Å. However, examination of the thermal parameters in Table 4.3.2 shows atoms C(7) and C(9) to have U_{22} values of 0.18 and 0.21 $Å^2$ respectively, while atoms C(6), C(8) and C(10) have U_{22} values of 0.06, 0.05 and 0.04 $Å^2$ respectively. The anomalously large U_{22} values for atoms C(7) and C(9) are in a direction (along $\underline{b}$) which is approximately normal to the plane of the glutarate chain, and can be explained if the glutarate chain is considered to be slightly disordered, adopting the two conformations (a) and (b) in Figure 4.3.3 ; atoms C(6), C(8) and C(10) have the same positions in both conformations, while atoms C(7) and C(9) are alternatively above and below the plane of the glutarate chain.

The acid anion (R_1) is non-planar, with a dihedral angle about C(2) - C(3) of about 55°. However, atoms C(2), C(3), C(4) and C(5) approach coplanarity with a dihedral angle about C(3) - C(4) of 176.1°. Details of the other conformations in the glutarate residues are given in

Table 4.3.9.

The interatomic distances and angles of the three hydrogen bonds are set out in Tables 4.3.10a and 4.3.10b respectively. The bond between The R_1 residues O(4) ····· O(3^{II}) is the strongest, although its O ····· H ····· O angle is the least favourable of the three. Its length (2.49 Å) is not significantly different from that found for a similar bond in ammonium hydrogen diacetate.[11] The bond between O(1) and O(2) which joins the anion and the acid molecule is in a similar environment and its O ····· H ····· O angle is 177.5°; however it is significantly weaker, with an O ····· O distance of 2.57 Å. The third bond {O(5) ····· O(6)} is between the unionised carbonyl group of the acid anion and the other carbonyl group of the acid molecule and its length of 2.64 Å is similar to those found in carboxylic acid dimers. The O-H distances in the three bonds - 1.08, 1.06 and 0.96 Å - show the expected increase with decreasing O ····· O distance and points representing these O-H distances and the corresponding O ···· O distances show a good fit to the Hamilton-Ibers version of the Nakamoto-Margoshes-Rundle curve (Figure 4.2.4). The two shorter hydrogen bonds make angles with both the donor and acceptor bonds which are close to tetrahedral (110-117°), whereas the angle of the longest hydrogen bond with the acceptor groups differs appreciably from this value (136.8°).

The environment of the potassium ion is represented in Figure 4.3.4; the ion is co-ordinated to 8 oxygen atoms at distances of less than 3.04 Å and the K^+ ····· O distances and O ····· K^+ ····· O angles

are given in Tables 4.3.11 and 4.3.12.

As a further test of the applicability of the symbolic addition method to neutron data, an attempt was made to solve the structure of potassium tri-hydrogen di-glutarate directly from neutron data, and with hydrogen accounting for 22 per cent of the total scattering power of the crystal, compared with 20 per cent in potassium tri-hydrogen di-succinate, this was a slightly stiffer test of the method. However, the results were equally successful; phases were found for 191 reflections with $E \geq 1.5$ and an E-map calculated with these phased E's as coefficients revealed every atom in the structure, although a few of the methylenic hydrogens were poorly resolved.

TABLES AND DIAGRAMS

Table 4.3.1

Fractional coordinates ($\underline{x}$, $\underline{y}$, $\underline{z}$) and absolute orthogonal coordinates (in A, with $\underline{X}' = \underline{a}x\sin\beta$, $\underline{Y} = \underline{b}y$, $\underline{Z}' = \underline{c}z + \underline{a}x\cos\beta$, and with standard deviations in parentheses).

(a) Neutron analysis.

	$\underline{x}$	$\underline{y}$	$\underline{z}$	$\underline{X}'$	$\underline{Y}$	$\underline{Z}'$
K^+	0.1208	0.4205	0.4307	1.350(11)	5.352(12)	3.993(12)
O(1)	0.0718	0.3022	0.8282	0.802(8)	3.847(11)	7.766(8)
O(2)	0.2308	0.2957	0.6404	2.578(9)	3.764(10)	5.911(9)
O(3)	0.2592	0.1317	0.7095	2.895(8)	1.676(8)	6.546(9)
O(4)	0.6017	0.4786	0.7891	6.721(9)	6.091(9)	7.113(9)
O(5)	0.6617	0.4508	0.5716	7.391(9)	5.734(9)	5.031(8)
O(6)	0.6769	0.3967	0.3026	7.561(9)	5.049(13)	2.488(9)
O(7)	0.8712	0.4295	0.3192	9.731(10)	5.467(13)	2.541(10)
O(8)	0.9671	0.3873	-0.3413	10.800(11)	4.931(11)	-3.740(10)
C(1)	0.2859	0.2103	0.6374	3.193(7)	2.676(7)	5.853(6)
C(2)	0.3858	0.2026	0.5367	4.309(7)	2.578(8)	4.850(7)
C(3)	0.4631	0.3006	0.5263	5.172(8)	3.826(8)	4.711(6)
C(4)	0.5135	0.3342	0.6673	5.736(7)	4.253(7)	6.012(7)
C(5)	0.5991	0.4272	0.6700	6.691(7)	5.436(7)	5.991(7)
C(6)	0.7814	0.4072	0.2517	8.727(8)	5.183(9)	1.953(7)
C(7)	0.7793	0.3750	0.0941	8.704(9)	4.772(16)	0.469(8)

Table 4.3.1(a) (cont'd)

	x	y	z	X'	Y	Z'
C(8)	0.8919	0.3819	0.0214	9.961(8)	4.861(7)	-0.277(8)
C(9)	0.8745	0.3490	-0.1304	9.767(9)	4.442(17)	-1.698(9)
C(10)	0.9754	0.3476	-0.2242	10.895(7)	4.423(8)	-2.636(8)
H(1)	0.6619	0.5441	0.7822	7.393(17)	6.924(14)	7.015(14)
H(2)	0.1376	0.2025	0.2517	1.537(11)	3.786(16)	7.009(13)
H(3)	0.6733	0.4150	0.4013	7.521(18)	5.281(20)	3.421(17)
H(4)	0.4483	0.3624	0.0658	5.007(13)	1.729(15)	5.091(25)
H(5)	0.6584	0.6818	0.0639	3.815(23)	2.313(27)	3.926(17)
H(6)	0.5924	0.8602	0.0217	4.552(19	4.584(18)	4.289(18)
H(7)	0.4630	0.7800	0.0444	5.998(20)	3.562(19)	4.006(19)
H(8)	0.4450	0.1453	0.2438	4.970(25)	4.514(34)	6.770(21)
H(9)	0.5693	0.2316	0.2180	6.358(26)	3.416(22)	6.461(25)
H(10)	0.7001	0.3944	0.0407	7.820(21)	5.019(36)	0.008(15)
H(11)	0.7551	0.2919	0.1036	8.434(26)	3.715(30)	0.571(31)
H(12)	0.9678	0.3531	0.0775	10.807(23)	4.494(40)	0.212(21)
H(13)	0.9121	0.4567	0.0246	10.187(59)	5.812(42)	-0.257(45)
H(14)	0.7974	0.1239	0.3213	8.906(34)	4.786(57)	-2.112(24)
H(15)	0.8370	0.2245	0.3668	9.349(39)	3.504(45)	-1.704(35)

Table 4.3.1 (cont'd)

(b) X-ray analysis.

	x	y	z	X'	Y	Z'
K^+	0.1221	0.4180	0.4337	1.368(2)	5.305(2)	4.027(2)
O(1)	0.0721	0.3000	0.8237	0.808(8)	3.808(10)	7.734(9)
O(2)	0.2291	0.2937	0.6373	2.567(8)	3.728(8)	5.871(8)
O(3)	0.2623	0.1316	0.7103	2.940(7)	1.670(8)	6.562(8)
O(4)	0.5984	0.4774	0.7844	6.706(8)	6.058(8)	7.081(8)
O(5)	0.6607	0.4480	0.5718	7.403(8)	5.685(8)	5.040(8)
O(6)	0.6782	0.3968	0.3024	7.599(10)	5.035(12)	2.489(10)
O(7)	0.8719	0.4291	0.3218	9.770(10)	5.446(12)	2.568(11)
O(8)	0.9684	0.3864	-0.3411	10.852(9)	4.904(9)	-3.740(9)
C(1)	0.2862	0.2079	0.6350	3.207(9)	2.639(9)	5.838(10)
C(2)	0.3857	0.1996	0.5341	4.322(13)	2.533(12)	4.833(14)
C(3)	0.4618	0.2986	0.5240	5.175(11)	3.790(12)	4.696(13)
C(4)	0.5138	0.3312	0.6676	5.757(10)	4.202(12)	6.024(12)
C(5)	0.5955	0.4259	0.6666	6.674(10)	5.406(11)	5.970(11)
C(6)	0.7844	0.4050	0.2488	8.490(13)	5.140(15)	1.925(13)
C(7)	0.7781	0.3786	0.0971	8.720(14)	4.804(20)	0.497(13)
C(8)	0.8957	0.3791	0.0242	10.036(13)	4.811(15)	-0.254(14)
C(9)	0.8737	0.3559	-0.1293	9.791(14)	4.517(28)	-1.691(16)
C(10)	0.9762	0.3505	-0.2244	10.939(11)	4.448(11)	-2.643(12)

Table 4.3.2 (a) (Neutron analysis)

Vibrational parameters ($\mathring{A}^2 \times 10^4$), with standard deviations in parentheses.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K^+	164(47)	219(57)	298(63)	37(47)	70(46)	11(49)
O(1)	294(38)	822(69)	252(40)	27(46)	123(34)	230(45)
O(2)	358(42)	402(45)	472(52)	70(39)	147(39)	228(41)
O(3)	311(37)	223(34)	452(47)	125(34	193(36)	101(34)
O(4)	416(47)	440(51)	407(48)	-251(42)	273(40)	-231(41)
O(5)	414(43)	442(48)	204(36)	-99(40)	128(34)	-8(36)
O(6)	366(44)	955(83)	290(45)	-103(53)	127(37)	-225(51)
O(7)	424(48)	904(80)	336(46)	-123(58)	56(40)	-150(54)
O(8)	531(55)	550(60)	448(54)	144(52)	25(46)	121(47)
C(1)	326(31)	277(31)	212(32)	-73(30)	-11(27)	42(28)
C(2)	417(39)	316(36)	364(38)	-4(33)	209(34)	-81(32)
C(3)	396(36)	406(40)	196(32)	-18(35)	133(28)	26(30)
C(4)	411(39)	322(36)	233(34)	-102(33)	66(31)	47(28)
C(5)	299(31)	220(31)	295(33)	2(29)	49(27)	40(29)
C(6)	463(40)	615(52)	212(34)	-36(42)	99(31)	-97(36)
C(7)	360(43)	1,767(123)	251(41)	213(63)	123(35)	-15(57)
C(8)	454(42)	544(49)	334(39)	-208(38)	189(34)	-126(36)
C(9)	252(38)	2,097(147)	316(43)	219(63)	96(34)	-213(66)
C(10)	252(34)	446(44)	379(39)	55(33)	150(30)	-84(34)
H(1)	740(98)	364(71)	402(75)	-86(73)	359(75)	-143(62)

Table 4.3.2(a)(cont'd)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
H(2)	412(68)	516(76)	285(64)	-164(65)	136(56)	2(58)
H(3)	557(90)	812(12)	552(93)	-271(97)	140(77)	-202(91)
H(4)	688(114)	165(65)	1,477(179)	-89(72)	582(124)	170(86)
H(5)	911(142)	1,472(209)	257(77)	427(146)	29(85)	534(112)
H(6)	644(102)	497(96)	604(99)	-7(85)	-216(83)	-213(81)
H(7)	751(117)	614(111)	747(110)	221(100)	444(98)	167(94)
H(8)	906(144)	1,779(269)	561(115)	477(167)	489(118)	136(147)
H(9)	1,070(169)	617(131)	966(158)	-50(125)	-285(134)	-444(120)
H(10)	596(109)	2,472(331)	128(69)	116(162)	-81(71)	-185(123)
H(11)	881(150)	977(175)	1,354(212)	-329(147)	400(147)	-410(171)
H(12)	607(114)	2,566(372)	546(116)	842(179)	-67(93)	302(165)
H(13)	3,326(611)	1,505(312)	1,914(346)	-1432(373)	1624(396)	-1382(292)
H(14)	1,114(217)	3,454(630)	531(129)	-1295(325)	-40(134)	-109(232)
H(15)	1,830(321)	2,591(428)	1,487(266)	1802(339)	1144(259)	1817(316)

Table 4.3.2 (b)(x-ray analysis)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
K(1)	498(11)	502(10)	504(15)	-46(19)	330(19)	-141(19)
O(1)	594(46)	959(63)	632(59)	-415(89)	322(78)	-286(83)
O(2)	570(42)	645(45)	622(54)	-429(73)	451(73)	-126(67)
O(3)	536(40)	605(43)	634(52)	-472(70)	485(70)	-110(63)
O(4)	635(46)	697(48)	588(54)	271(75)	471(76)	224(74)
O(5)	583(42)	617(43)	567(52)	94(69)	458(70)	285(65)
O(6)	747(59)	1,441(90)	634(67)	299(111)	481(94)	450(113)
O(7)	787(61)	1,180(80)	789(71)	211(112)	66(96)	407(108)
O(8)	727(54)	689(49)	738(63)	-372(83)	360(86)	-439(79)
C(1)	455(50)	446(47)	444(65)	-58(78)	181(81)	106(74)
C(2)	802(78)	597(63)	723(89)	103(110)	960(135)	423(109)
C(3)	448(53)	780(74)	666(84)	-59(113)	494(102)	349(98)
C(4)	508(58)	698(66)	557(78)	-54(108)	16(96)	277(94)
C(5)	395(46)	619(57)	461(69)	64(90)	156(80)	-78(81)
C(6)	764(75)	940(93)	533(86)	232(124)	459(113)	292(129)
C(7)	683(79)	1,739(155)	397(87)	330(161)	543(118)	97(167)
C(8)	645(69)	1,034(96)	522(85)	67(129)	540(114)	226(125)
C(9)	596(76)	2,356(246)	515(104)	503(239)	465(134)	-91(214)
C(10)	567(60)	545(56)	537(74)	30(92)	370(97)	-48(88)

Table 4.3.3

Observed structure amplitudes and final calculated structure factors. (×10)

0,0,L

2	89	-96
4	50	-49
6	111	113

0,1,L

1	45	49
2	66	-78
3	46	-42
4	51	-48
5	23	23
6	78	-82
9	90	-91

0,2,L

2	43	-46
3	74	-80
4	35	30
5	64	68
6	70	-76
7	46	-43
8	46	-45

0,3,L

1	40	30
6	28	29
9	35	42

0,4,L

0	82	-92
2	66	76
5	24	-27
7	31	23

0,5,L

3	73	70
4	54	-47
5	44	-34
6	59	59

0,6,L

1	42	-42
5	28	-24
7	35	-36
8	27	23

0,7,L

1	41	-36
3	30	28
4	42	-33
5	39	-35
7	43	35
8	37	-28

0,8,L

0	60	-54
1	74	-81
2	50	-42
3	34	36
4	37	35
5	38	-37
6	47	-47

0,9,L

1	55	-55
2	38	41
5	29	-31
7	28	16

0,10,L

0	70	68
1	31	25
2	33	31
5	34	-37
6	31	44

0,11,L

2	28	-24
3	24	-20
4	44	-41
5	33	42

0,12,L

2	42	-42
5	29	28

0,13,L

2	30	33

0,14,L

0	30	27

1,0,L

-10	63	66
-8	60	59
-4	35	-39
2	63	-60
4	52	54
6	49	-46

1,1,L

-10	24	21
-8	47	-43
-6	81	-86
-5	23	-21
-4	29	32
-3	49	-47
-2	77	-98
-1	12	-10
0	23	-25
1	17	-15
2	58	55
3	70	60
4	71	62
8	48	43

1,2,L

-10	30	-27
-9	36	-36
-7	65	-61
-6	35	31
-5	65	64
-4	43	-39
-3	79	-69
-2	32	-35
0	24	-17
2	101	108
3	21	-17
4	47	41
5	94	95
7	40	40
8	35	32
9	42	-37

1,3,L

-10	30	25
-9	29	29
-8	52	49
-6	56	57
-5	56	64
-3	48	-43
-2	38	-39
-1	50	48
1	27	25
2	39	-32
3	28	-27
4	23	-22
5	41	32

1,4,L

-10	24	19
-8	34	-34
-1	66	-68
0	92	-100
1	76	73
2	60	-55
4	69	-62
6	44	45
8	45	-45
9	41	-50

1,5,L

-10	32	34
-8	67	-67
-5	44	-41
-4	25	-17
-3	41	41
-2	64	-64
1	38	36
2	67	-61
4	73	73
5	59	52
-7	38	-38

1,6,L

-5	53	-48
-4	30	23
-3	62	61
-2	30	23
0	27	-24
1	84	86
2	48	-38
4	45	-38
5	49	-49
7	28	27

1,7,L

-8	69	-72
-7	28	21
-6	59	-56
-5	31	25
-3	82	83
-2	69	-74
-1	47	-42
2	51	51
3	82	-82

1,8,L

-7	42	-37
-6	56	55
-3	35	42
-1	25	-17
0	77	79
2	43	43
3	45	45
4	63	60
5	48	-53

1,9,L

-9	26	-21
-8	29	26
-6	41	43
-5	29	28
-3	36	-35
-2	103	113
-1	30	29
0	39	41
1	27	22
3	58	-66
4	44	-41

1,10,L

-5	52	-50
-4	49	-42
-2	41	33
-1	36	32
0	31	-30
2	54	-43
4	65	-58
5	33	32

1,11,L

-7	27	-29
-4	24	-18
0	42	-41
1	22	-21
2	40	-41
3	37	27
4	73	76
5	25	-17

1,12,L

-5	37	-34
-4	43	33
-3	42	43
-2	23	-16
2	65	59
6	42	-36

1,13,L

-6	35	34
-3	34	34
-2	21	-19
0	32	38
2	34	-29
5	29	-24

1,15,L

0	23	-21
1	28	20

2,0,L

-10	46	-43
-8	78	-80
-4	23	-23
4	38	39

2,1,L

-8	115	129
-7	59	65
-6	30	30
-5	41	-31
-4	68	65
-2	36	-27
-1	67	72
0	36	35
1	42	-34
2	73	69
3	33	-29
5	28	-36
6	37	-38

2,2,L

-10	35	-26
-8	55	55
-4	32	-23
-3	44	-42
-2	48	44
-1	73	81
2	71	-68
4	44	-35
7	38	-32

2,3,L

-8	76	76
-7	41	-36
-5	21	13
0	54	-52
1	56	-46
3	34	32
4	37	31
6	30	30

2,4,L

-10	23	29
-9	43	40
-7	24	-25
-6	36	-27
-4	63	65
-3	59	-54
-2	23	-21
-1	41	-33
3	21	20
6	78	-77
7	52	56

2,5,L

-8	43	-37
-7	60	54
-6	43	47
-3	72	79
0	60	-49
1	35	-34
3	22	18
5	43	41
8	46	43

2,6,L

-9	66	65
-8	30	-29
-6	28	-23
-5	68	63
-4	45	43
-2	55	-59
-1	40	-41
0	57	54
1	74	72
3	30	-29
4	23	22
5	66	65
7	43	-34

2,7,L

-7	56	-55
-5	42	41
-3	69	-69
0	54	-50
-1	22	-20
1	48	54
5	74	-73

2,8,L

-8	30	32
-6	30	-23
-5	28	23
-2	37	-27
-1	27	23
0	35	-41
2	36	31
4	51	-57
5	26	25

2,9,L

-9	40	46
-6	29	-35
-4	41	-49
0	49	-36
4	34	-34
5	30	-30
6	67	62

2,10,L

-8	33	-34
-7	30	-27
-6	40	-38
2	86	90
3	49	-44

2,11,L

-6	44	40
-4	46	45
-2	27	19
-1	31	24
0	43	45
2	61	64
4	23	-21

2,12,L

0	46	47
2	38	-36

2,13,L

-5	24	-30
-4	37	-34
-2	41	43
2	33	-30

2,14,L

3	24	19
4	37	42

2,15,L

-1	26	23

3,0,L

-10	28	28
-8	67	-68
-6	21	22
-4	76	70
-2	108	-123
2	27	-25
4	31	-26
6	24	-22
8	39	42

3,1,L

-11	34	32
-8	26	33
-5	26	-23
-3	32	30
-2	60	-59
-1	50	-50
0	66	68
1	87	92
2	45	-39
4	66	-63
5	23	-23
6	86	83
7	47	-48
8	33	31
9	23	-15

3,2,L

-9	58	-58
-8	46	-41
-5	33	31
-4	70	-67
-3	61	-55
-2	62	70
-1	56	51
0	27	-27
1	64	-64
4	22	23
5	66	-67
6	49	49
7	57	50
8	31	-23
9	24	-25

3,3,L

-10	24	-18
-8	28	-28
-7	39	-41
-6	61	63
-5	31	31
-4	65	66
-2	41	34
-1	29	29
0	81	80
3	36	-32
4	28	25
5	59	49
6	97	98
7	34	44
8	69	-69

Table 4.3.3 (cont'd)

3,4,L

-9	26	23
-8	27	20
-7	59	58
-6	55	60
-4	47	-44
-3	72	70
-2	45	49
-1	80	85
0	53	44
1	63	-63
2	71	64
3	105	-105
6	84	-84
7	38	-33

3,5,L

-10	33	-33
-7	68	-64
-6	31	27
-5	77	-86
-4	62	-64
-3	34	26
-2	21	23
-1	27	-32
0	60	-59
1	79	-77
2	56	-52
4	44	-45
7	28	-26

3,6,L

-9	65	-76
-7	21	-11
-6	28	-29
-5	38	37
-4	53	52
-3	47	-53
-2	21	18
-1	35	29
2	36	-38
3	35	35
4	26	26
5	49	45
6	57	-61

3,7,L

-7	82	75
-6	49	-44
-5	24	18
-4	41	45
-3	30	24
-2	67	-65
-1	30	24
1	32	28
2	38	-42
3	25	-18
4	55	-59
5	51	-55
6	49	-38

3,8,L

-6	33	-32
2	35	-35
3	37	40
5	51	-46
6	49	49

3,9,L

-7	30	28
-6	26	-30
-4	79	82
-1	24	16
0	52	55
1	27	-20
2	33	36
3	37	-30
4	65	59
5	44	44

3,10,L

-6	55	61
-5	46	-49
-3	32	32
-2	52	-53
-1	26	-30
1	30	-23
3	53	59
4	32	-41
5	32	-34

3,11,L

-4	44	-40
-1	53	-56
1	30	26

3,12,L

-2	24	21
2	34	-25
4	33	43

3,13,L

-4	29	22
-1	22	-24
2	37	37

3,14,L

-2	41	-38

4,0,L

-10	30	-26
-8	49	48
-6	37	-39
-4	18	12
-2	60	-56
2	100	-101
4	20	23
6	22	-16
8	70	70

4,1,L

-7	89	89
-6	33	-25
-5	40	-35
-4	44	-41
-3	45	-50
-2	84	85
1	24	29
2	52	-48
4	95	101
5	35	37
6	62	54
8	24	-29

4,2,L

-8	55	57
-7	67	66
-2	27	24
-1	49	46
0	75	-73
1	37	36
2	49	53
3	37	-33
4	36	34
5	49	-44
6	32	-32
7	62	-62

4,3,L

-9	63	62
-8	63	-64
-7	84	-80
-6	61	54
-4	47	-47
-2	26	-23
-1	38	-37
0	47	-45
2	48	-46
3	23	-23
5	27	-27
7	44	-41

4,4,L

-8	64	68
-7	67	-66
-5	54	-59
-3	38	33
-1	76	-82
0	20	-24
1	37	37
2	88	81
3	31	26
4	62	-59
5	36	37
6	63	67
7	37	-29

4,5,L

-10	35	32
-9	32	-33
-8	22	-20
-7	46	-39
-5	46	47
-3	49	-46
-1	55	57
2	49	51
3	26	-27
6	69	-73

4,6,L

-9	26	26
-8	58	-69
-7	20	16
-6	37	36
-5	40	38
-4	23	16
-3	41	32
-1	47	42
0	50	52
1	27	22
6	47	41

4,7,L

-6	51	-58
-3	28	-22
-2	30	34
2	29	21
3	45	-49
4	43	42
6	39	-36
7	28	30

4,8,L

-8	46	-50
-7	26	-23
-5	65	-66
-1	38	-27
0	29	26
2	22	-13
3	44	49
4	33	-33

4,9,L

-5	52	60
-4	43	-50
-2	52	-44
0	22	14
1	49	47
2	35	-31
3	26	19

4,10,L

-4	23	-29
-3	30	-27
1	48	49
3	46	-48
4	29	-30

4,11,L

-2	43	45
-1	31	29
3	30	-29
4	34	31
6	35	32

4,12,L

-2	26	35
3	35	-34

4,13,L

-5	35	-33
-3	24	19
1	31	-27

4,14,L

2	26	-25

5,0,L

-10	37	41
-8	26	-25
-6	66	-66
-4	84	83
-2	31	-28
2	29	-22
6	94	-87
8	40	38

5,1,L

-10	24	-22
-8	30	26
-7	45	45
-6	43	-44
-3	64	63
-2	27	25
-1	45	-42
0	80	-82

5,2,L

-10	32	-32
-7	48	51
-6	66	66
-4	23	17

5,3,L

0	82	-82
2	29	-25
3	76	-83
5	50	-48
6	30	-23
7	80	79

5,4,L

-7	96	102
-4	24	30
-3	64	66
-2	82	71
-1	34	38
0	91	91
1	22	-23
2	31	-27
3	38	36
4	27	31
5	46	43
6	60	61
7	59	-56

5,5,L

-8	25	29
-7	45	57
-6	54	54
-5	55	-54
-4	54	-50
-3	60	-55
0	60	-55
1	53	-53
5	33	-33
7	39	-34

5,6,L

-8	27	-20
-7	65	-72
-5	84	-80
-3	34	-32
0	23	-20
1	53	-50
2	27	28
4	52	52
6	54	-48

5,7,L

-5	40	-43
-4	47	48
-3	98	107
-2	35	-34
-1	49	-50
0	48	-50
1	40	35
3	46	44
5	28	30
6	26	24

5,8,L

-5	88	101
-4	60	-70
-3	36	-34
-2	38	-37
3	29	28
5	39	-44

5,9,L

-6	28	-32
-3	56	-53
-2	25	-24
-1	36	34
0	26	27
2	47	45
4	41	-41

5,10,L

-6	35	-41
-4	29	23
-3	30	-30
1	33	-30
3	32	-19

5,11,L

0	45	-47
1	21	-24
2	23	16

5,12,L

-4	29	21

5,13,L

0	39	38

6,4,L

-6	36	-38
-4	26	-30
-2	69	66
0	20	-12
3	72	-76
4	31	22
5	45	-45
7	31	37

6,5,L

-9	26	-25
-8	44	-40
-6	39	38
-5	86	-90
-2	31	29
-1	34	34
0	40	40
4	49	-45
5	83	83

6,6,L

-7	45	-41
-6	35	40
-5	40	37
-4	62	-66
-3	75	77
-1	56	-46
1	53	48
2	23	-17
3	36	35
4	34	28

6,7,L

-7	49	57
-6	26	34
-4	30	20
-3	28	-25
-2	45	45
0	22	-20
1	46	45
0	26	-20

6,10,L

0	50	-49

6,11,L

1	32	-30

6,12,L

-3	26	29
0	23	22
1	35	27
2	31	-35

6,13,L

-1	25	-18

7,0,L

-6	66	61
-2	66	-69
0	50	-36
2	41	36
4	59	-61

Table 4.3.3 (cont'd)

7,1,L

-7	29	27
-6	34	-29
-5	28	-30
-4	36	-30
-3	28	-21
-2	90	-91
-1	30	28
0	22	17
3	42	38

7,2,L

-8	26	26
-4	26	22
2	39	-37
3	35	-34
5	61	-63
6	38	42
7	33	28

7,3,L

-3	82	-83
-2	65	-65
-1	45	47
0	24	-15
4	36	34
6	29	-30
7	25	21

7,4,L

-9	43	45
-8	22	24
-7	56	-58
-6	67	-68
-3	47	41
-1	83	85
2	22	19
3	86	88
5	42	54
6	25	17

7,5,L

-9	49	46
-5	82	81
-4	42	-38
-3	54	56
-2	100	110
-1	42	-45
0	35	-34
1	33	-29
2	44	46

7,6,L

-6	54	-59
-4	43	50
-3	71	-63
-1	108	-117

7,7,L

-5	67	-73
-1	23	-18
2	37	35

7,8,L

-5	25	-25
-4	35	36
-3	30	28
-1	23	24

7,9,L

-7	27	-22
-4	29	21
-2	44	-43

7,10,L

-2	35	31
2	28	34
3	29	-30

7,11,L

-4	50	-55
1	25	26
2	36	-28
3	27	-25
5	23	-18

7,12,L

-3	31	-40
-2	41	49

8,0,L

-8	64	-62
-6	69	66
-4	29	31
-2	65	69
0	106	113
2	55	-50
4	34	-29

8,1,L

-9	56	-53
-8	28	25
-6	92	83
-3	35	30
-1	96	-102
1	72	69
2	23	-25
3	34	-44
4	39	37

8,2,L

-8	51	-46
-5	79	-77
-4	31	28
-2	32	-28
-1	89	92
1	60	66
4	29	-29
5	26	32

8,3,L

-9	51	53
-6	60	63
-5	26	26
-4	53	-48
-3	57	62
-2	45	-44
-1	78	78
0	22	-25
1	26	-26
4	38	-34
6	34	36

8,4,L

-7	25	24
-5	56	50
-4	35	-38
-3	79	-80
-1	56	52
0	60	458
3	31	-22
4	32	36

8,5,L

-5	34	34
-3	56	-51
-2	21	-11
0	21	12

8,6,L

-4	60	-60
2	52	-51
3	26	-24
4	37	43

8,7,L

-7	35	33
-6	29	-20
-5	42	-42
-4	38	40
-3	43	48
-1	25	-16
2	28	-20
3	37	38
4	25	19
5	24	26

8,8,L

-1	29	-30
1	56	-57

8,9,L

-4	34	32
-1	44	-40

8,10,L

1	23	24
2	46	52

9,0,L

-8	33	32
-4	30	-32
-2	72	77
4	29	34

9,1,L

-7	42	-47
-2	78	-75
0	24	22
1	36	35
2	24	-30
4	53	-54

9,2,L

-7	25	-22
-6	43	-32
-5	26	-16
-3	29	28
-1	59	-59
0	38	32

9,3,L

-4	51	49
-3	48	-48
-2	22	16
-1	72	76
1	79	-77
2	39	35
4	36	-42

9,4,L

-6	21	-15
0	50	-52
1	58	58
3	23	-16
4	29	-23

9,5,L

-7	45	38
-2	25	25
-1	55	54

9,6,L

-6	29	24
-3	53	57
-2	28	21
1	42	-42
3	25	-24
4	27	-32

9,7,L

-7	39	-37
-5	28	30
-1	80	-74
0	25	30
-1	76	-74
0	33	30
2	37	-39

9,8,L

-5	36	42
-3	27	-26
-1	26	18
3	33	22
5	30	-22

9,9,L

-3	29	-29
-2	35	24

9,10,L

-2	23	-23
-1	26	37
3	24	-23

9,11,L

-2	23	19

10,0,L

-6	23	-27
-4	74	-81
0	54	54
2	28	-32
4	51	57

10,1,L

-7	31	33
-4	31	29
-3	49	-53
0	95	97
1	30	-29
2	34	-33

10,2,L

-6	30	26
-4	24	19
-2	53	-53
-1	36	-29
1	38	-42
3	42	46
5	25	24

10,3,L

-7	27	27
-2	41	-46
-1	34	35
0	36	34
2	32	-35
3	49	43
4	26	17

10,4,L

-7	51	53
-3	56	-56
-1	47	49
3	73	-76

10,5,L

-5	44	-43
-4	31	-37
-3	56	59
-1	31	-35
4	26	22

10,6,L

-2	22	28
3	42	47

10,7,L

-2	30	28
5	23	-17

10,8,L

-5	29	-27
-4	37	43
-1	32	38
2	29	29

10,9,L

-3	30	31
1	26	-19

11,0,L

-6	23	19
-4	38	40
-2	60	63
0	52	-59
2	20	23
4	27	21

11,1,L

-6	49	51
-3	33	37
-2	59	-60
-1	36	-34
2	45	-50
3	30	27
5	29	-36

11,2,L

-5	28	28
-1	27	-27
0	31	-38
2	24	24
5	31	-29

11,3,L

-6	46	43
-4	21	-14
0	37	39
1	27	-31

11,4,L

-6	29	23
-4	38	-32
-3	25	-20
0	27	29
1	33	-36
2	39	-33

11,5,L

-5	49	43
-1	31	-30
0	35	-39
1	38	30

11,6,L

-5	40	42

11,7,L

-1	31	32

11,8,L

-3	39	46

12,0,L

0	36	-38
4	36	36

12,2,L

-5	41	-36
-3	21	19
1	29	-21

12,3,L

-4	25	19
-2	56	55
0	31	-31

12,4,L

-3	28	28
2	29	19

12,5,L

-3	29	-32
-1	28	29

12,6,L

-1	43	46
1	23	-29

13,0,L

2	29	22

13,1,L

-1	45	-44
1	28	26

13,2,L

-2	28	-25
0	27	-29
2	22	-26

Table 4.3.4

Analysis of structure-amplitude agreement. ($\underline{N}$ is the number of reflections in each group).

(a) As a function of $(\sin\theta)/\lambda$

Range	ΣF_o	$\Sigma\Delta$	N	R	$(\Sigma\Delta)/N$
0.0 - 0.1	15.72	1.69	6	0.107	0.282
0.1 - 0.2	300.41	28.24	52	0.094	0.543
0.2 - 0.3	693.53	51.35	143	0.074	0.359
0.3 - 0.4	1092.65	83.24	233	0.076	0.357
0.4 - 0.5	1506.38	125.39	340	0.083	0.368
0.5 - 0.6	777.57	92.28	231	0.119	0.399
0.6 - 0.7	12.04	1.25	4	0.104	0.313

(b) As a function of F_o

0.0 - 4.0	1576.19	201.07	528	0.128	0.380
4.0 - 6.0	1434.85	109.26	295	0.076	0.370
6.0 - 8.0	916.39	49.73	134	0.054	0.372
8.0 -10.0	375.15	15.99	43	0.043	0.372
10.0 -12.0	95.73	7.40	9	0.077	0.820
All	4398.31	383.45	1009	0.087	0.380

Table 4.3.5.

Equivalent positions

I	x, y, z = C.C.U.
II	1-x, $\frac{1}{2}$+y, 3/2-z
III	1+x, y, -1+z
IV	1-x, $-\frac{1}{2}$+y, 3/2-z
V	-1+x, y, 1+z
VI	x, $\frac{1}{2}$-y, $-\frac{1}{2}$+z
VII	1-x, 1-y, -z
VIII	-1+x, y, z
IX	1-x, 1-y, 1-z

Table 4.3.6

Bond lengths (Å) in the glutarate residues: (a) neutron analysis, (b) x-ray analysis (Macdonald, 1971). Standard deviations are im parentheses.

		(a)	(b)
C(1)	- O(2)	1.250(12)	1.264(12)
C(1)	- O(3)	1.254(11)	1.239(12)
C(5)	- O(4)	1,299(11)	1,282(14)
C(5)	- O(5)	1.224(11)	1.212(13)
C(6)	- O(6)	1,290(12)	1.322(17)
C(6)	- O(7)	1.197(12)	1.211(17)
C(10)	- O(8)	1.214(12)	1.191(15)
C(10)	- $O(1^{III})$	1.299(11)	1.314(14)
C(1)	- C(2)	1.503(10)	1.505(17)
C(2)	- C(3)	1.524(11)	1.525(17)
C(3)	- C(4)	1.481(9)	1.507(17)
C(4)	- C(5)	1.521(10)	1.513(15)
C(6)	- C(7)	1.540(12)	1.469(19)
C(7)	- C(8)	1.465(12)	1.515(19)
C(8)	- C(9)	1.494(12)	1.487(21)
C(9)	- C(10)	1.466(12)	1.493(19)

Table 4.3.6 (cont'd)

C - H distances (neutron analysis only)

C(2) - H(4)	1.126(19)	C(7) - H(10)	1.027(22)
C(2) - H(5)	1.080(20)	C(7) - H(11)	1.096(34)
C(3) - H(6)	1.066(20)	C(8) - H(12)	1.045(26)
C(3) - H(7)	1.118(22)	C(8) - H(13)	0.978(44)
C(4) - H(8)	1.108(26)	C(9) - H(14)	1.015(37)
C(4) - H(9)	1.136(24)	C(9) - H(15)	1.025(46)

Table 4.3.7

Bond angles (degrees) in the glutarate residues: (a) neutron analysis, (b) x-ray analysis. Standard deviations are in parentheses.

	(a)	(b)
O(2) - C(1) - O(3)	123.5(0.8)	122.7(0.9)
C(2) - C(1) - O(3)	119.6(0.7)	119.7(0.9)
C(2) - C(1) - O(2)	116.9(0.7)	117.6(0.9)
C(1) - C(2) - C(3)	115.4(0.6)	114.6(0.9)
C(2) - C(3) - C(4)	111.8(0.6)	111.3(1.0)
C(3) - C(4) - C(5)	116.8(0.6)	114.9(0.9)
C(4) - C(5) - O(5)	124.0(0.7)	125.0(1.0)
C(4) - C(5) - O(4)	113.2(0.7)	112.4(0.9)
O(4) - C(5) - O(5)	122.8(0.8)	122.2(0.9)
O(6) - C(6) - O(7)	125.4(0.9)	121.5(1.2)
C(7) - C(6) - O(6)	111.0(0.7)	110.7(1.2)
C(7) - C(6) -O(7)	123.3(0.8)	127.8(1.3)
C(6) - C(7) -C(8)	117.5(0.8)	116.0(1.2)
C(7) - C(8) - C(9)	110.9(0.7)	109.6(1.1)
C(8) - C(9) - C(10)	120.8(0.8)	119.9(1.2)
C(9) - C(10) - O(8)	121.0(0.9)	120.9(1.2)
C(9) - C(10) - $O(1^{III})$	115.2(0.8)	117.1(1.2)
O(8) - C(10) - $O(1^{III})$	123.8(0.9)	121.9(1.1)

Table 4.3.7 (cont'd)

H - C - H angles (neutron analysis only)

H(4) - C(2) - H(5)	106.3(1.9)	H(10) - C(7) - H(11)	93.5(2.6)
H(6) - C(3) - H(7)	110.4(1.5)	H(12) - C(8) - H(13)	98.3(3.9)
H(8) - C(4) - H(9)	106.4(2.0)	H(14) - C(9) - H(15)	87.8(3.8)

Table 4.3.8

Sums of, and differences between, C - O distances, and differences between C - C - O angles in the carboxyl groups.

Neutron analysis

	R_1		R_2	
Carboxyl group	C(1)	C(5)	C(6)	C(10)
Σ(C-O), Å	2.504	2.523	2.487	2.513
Δ(C-O), Å	0.004	0.075	0.093	0.085
Δ(C-C-O), (deg.)	2.7	9.6	12.3	5.8

X-ray analysis

Σ(C-O), Å	1.503	1.494	1.533	1.505
Δ(C-O), Å	0.025	0.070	0.111	0.123
Δ(C-C-O), (deg.)	2.1	12.6	17.1	3.8

Table 4.3.9

Torsion angles* (degrees) in the glutarate residues : (a) Neutron analysis, (b) x-ray analysis, with standard deviations in parentheses.

Atom A	Atom B	Atom C	Atom D	Angle	
				(a)	(b)
C(1)	C(2)	C(3)	C(4)	55.0(0.6)	56.1(1.0)
C(2)	C(3)	C(4)	C(5)	176.1(0.6)	177.2(1.0)
C(6)	C(7)	C(8)	C(9)	-179.4(0.8)	-177.3(1.2)
C(7)	C(8)	C(9)	C(10)	-178.5(0.8)	-179.2(1.2)
O(2)	C(1)	C(2)	C(3)	39.4(0.7)	40.2(0.9)
O(3)	C(1)	C(2)	C(3)	-143.1(0.7)	-140.7(0.9)
C(3)	C(4)	C(5)	O(4)	153.6(0.7)	152.9(0.9)
C(3)	C(4)	C(5)	O(5)	-28.0(0.7)	-33.4(1.0)
O(6)	C(6)	C(7)	C(8)	-179.6(0.9)	-176.8(1.2)
O(7)	C(6)	C(7)	C(8)	5.9(0.8)	1.6(1.3)
C(8)	C(9)	C(10)	O(8)	-131.9(0.9)	-140.1(1.2)
C(8)	C(9)	C(10)	O(1)	44.8(0.9)	43.3(1.1)

*The angle A-B-C-D is defined as positive if when viewed along the B-C bond atom A has to be rotated clockwise to eclipse atom D.

Table 4.3.10(a)

Interatomic distances ($\mathring{A}$) in the hydrogen bonds : (a) neutron analysis, (b) x-ray analysis, with standard deviations in parentheses.

	(a)	(b)
O(1)···O(2)	2.569(13)	2.550(12)
O(1) - H(2)	1.056(16)	
H(2)···O(2)	1.514(16)	
O(4)···O(3^{II})	2.492(12)	2.513(11)
O(4) - H(1)	1.075(18)	
H(1)···O(3^{II})	1.421(17)	
O(6)···O(5)	2.640(12)	2.640(14)
O(6) - H(3)	0.962(20)	
H(3)···O(5)	1.678(19)	

Table 4.3.10(b)

Interatomic angles (degrees) in the hydrogen bonds (neutron analysis only), with standard deviations in parentheses.

O(1) - H(2)···O(2)	177.5(1.6)
C(10) - C(1) - H(2)	111.0(1.1)
C(10) - O(1)···O(2)	110.0(0.6)
O(4) - H(1)···O(3^{II})	173.3(1.5)
C(5) - O(4) - H(1)	109.1(1.1)
C(5) - O(4)···O(3^{II})	112.8(0.6)
O(6) - H(3)···O(5)	177.4(1.9)
C(6) - O(6) - H(3)	114.5(1.4)
C(6) - O(6)···O(5)	115.5(0.7)

Table 4.3.11

Environment of the potassium ion : oxygen contacts (Å) with standard deviations in parentheses.

	Neutron analysis	X-ray analysis
$K^+....O(2)$	2.776(15)	2.720(8)
$K^+....O(3^{VI})$	2.736(14)	2.763(8)
$K^+....O(8^{VII})$	2.753(16)	2.806(8)
$K^+....O(8^{V})$	2.847(16)	2.828(8)
$K^+....O(7^{VIII})$	2.938(14)	2.954(8)
$K^+....O(5^{IX})$	2.934(14)	2.975(8)
$K^+....O(1^{VI})$	3.037(16)	2.999(8)
$K^+....O(7^{IX})$	3.031(16)	3.013(8)

Table 4.3.12

Environment of the potassium ion : O···K···O angles (degrees). The standard deviations on the angles from the neutron analysis are ~ 0.5 deg.; from the x-ray analysis ~ 0.7 deg.

Neutron analysis

	O(2)	O(3^{VI})	O(8^{VIII})	O(8^{V})	O(7^{VIII})	O(5^{IX})	O(1^{VI})	O(7^{IX})
O(2)	0	99.0	150.0	69.0	131.1	89.2	76.1	79.1
O(3^{VI}	99.1	0	100.9	157.3	107.4	68.4	68.4	138.5
O(8^{VII})	150.9	101.1	0	98.2	62.4	77.6	132.5	71.1
O(8^{V})	69.6	158.6	97.8	0	71.2	128.3	89.7	60.2
O(7^{VIII})	131.3	107.7	61.5	70.9	0	138.5	76.6	104.2
O(5^{IX})	90.5	67.7	76.9	128.6	137.0	0	131.1	70.1
O(1^{VI})	77.2	68.3	130.5	91.1	76.2	131.4	0	146.4
O(7^{IX})	80.8	137.6	70.3	60.5	103.2	69.9	148.9	0

x-ray analysis

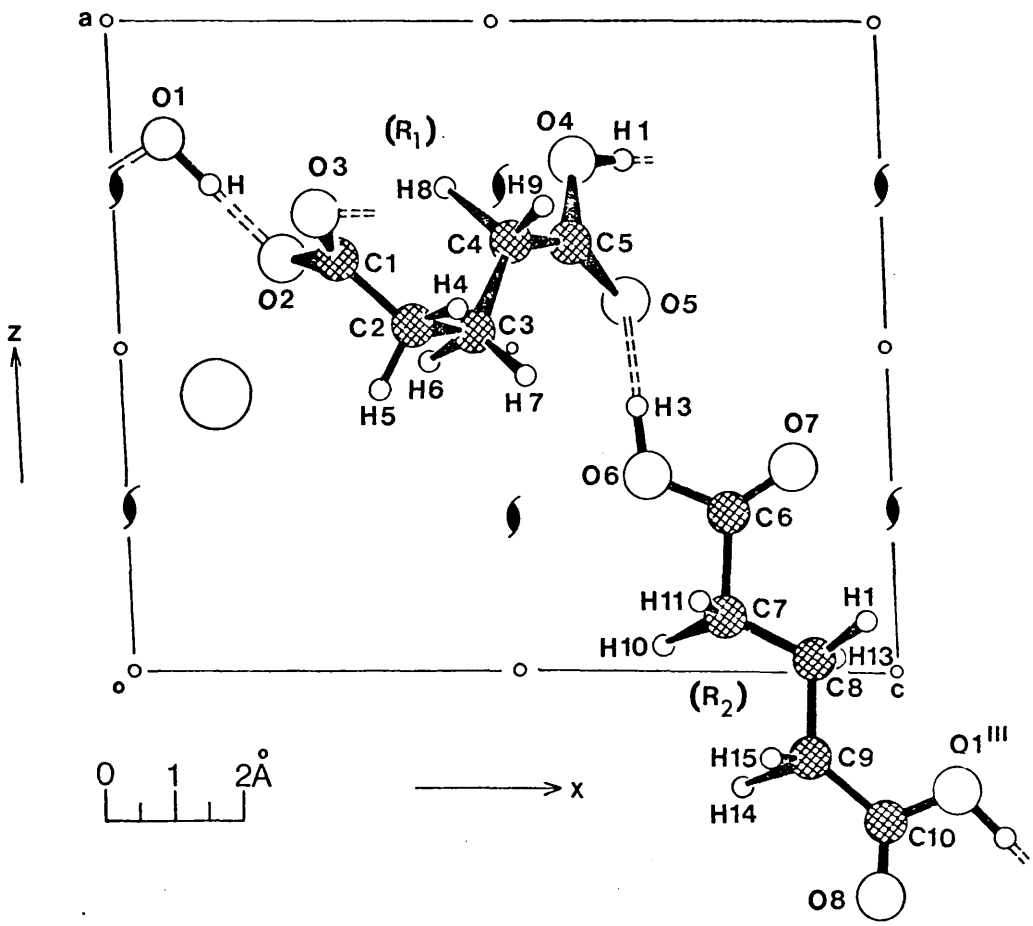


Figure 4.3.1 : KH_3Glut_2 - the crystal-chemical-unit (C.C.U.) and atomic numbering system.

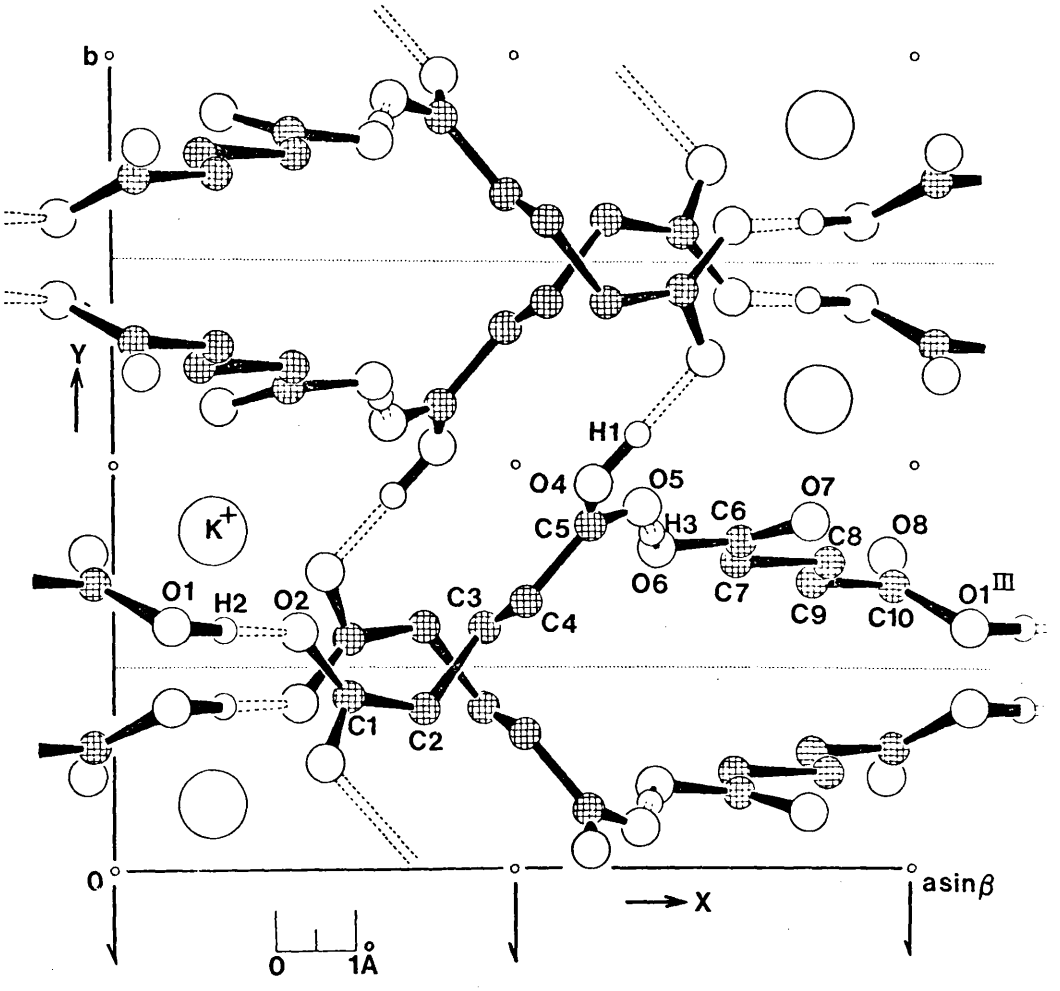


Figure 4.3.2 : The crystal structure of KH_3Glut_2 projected along the c axis. The methylenic hydrogen atoms have been omitted for clarity.

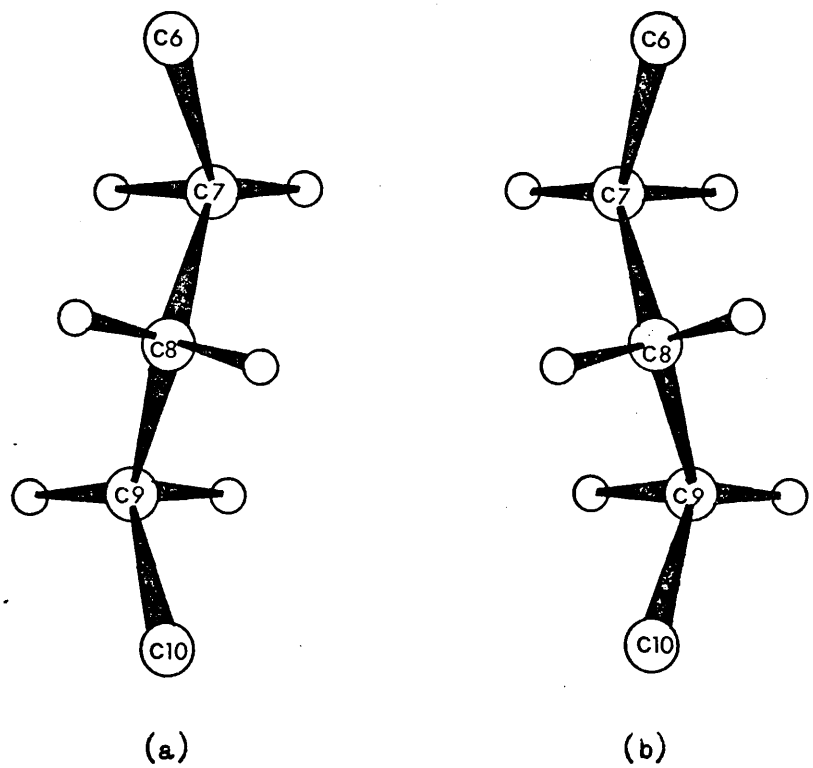


Figure 4.3.3 : The two disordered conformations proposed for the glutaric acid molecule (R_2)

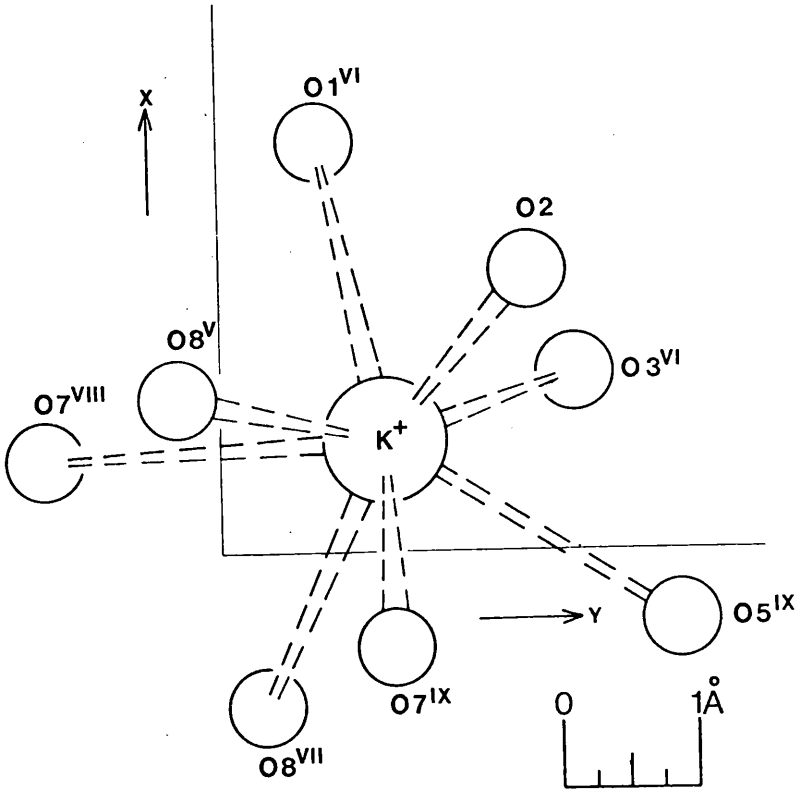


Figure 4.3.4 : The environment of the potassium ion in KH_3Glut_2.

References

1. H.N. Shrivastava and J.C. Speakman, J.Chem.Soc., 1151 (1961).
2. D.Hadži and A.Novak, Nuovo Cimento [X], 2 suppl., 715 (1955)
3. M.Currie, J.C.Speakman and N.A.Curry, J.Chem.Soc(A), 1862 (1967).
4. M.Currie, J.C.S. Chem. Comm., 17,972 (1972).
5. H.Marshall and A.T.Cameron, J.Chem.Soc., 91, 1519 (1907).
6. P.Groth, "Chemische Kristallographie", Vol. III, Engelman, Leipzig (1906).
7. S. K. Sikka, thesis, Bombay University (1969).
8. K.Nakamoto, M.Margoshes and R.E.Rundle, J.Chem.Phys., 77, 6480 (1955).
9. W.C.Hamilton and J.A.Ibers, "Hydrogen Bonding in Solids", Wiley, New York (1968).
10. A.L.Macdonald, Ph.D thesis, University of Glasgow (1971).
11. I.Nahringbauer, Acta. Chem. Scand., 23, 1653 (1969).

CHAPTER 5

THE CRYSTAL AND MOLECULAR STRUCTURE OF α-PICOLINE-N-OXIDE HYDROCHLORIDE MONOHYDRATE.

5.1. Introduction

The ability of many monobasic acids to form crystalline acid salts, $\underline{M}^{+}H\underline{X}_{2}^{-}$, which contain short, symmetrical hydrogen bonds (Type A acid salts) has been described in section 1 of Chapter 4; certain monoacidic bases are capable of forming analogous crystalline basic salts, $H\underline{B}_{2}^{+}\underline{X}^{-}$, where $\underline{X}^{-}$ is the acid anion, and $\underline{B}$ the neutral base.

In 1962 Hadzi[1] reported the preparation of such a basic salt, α-picoline N-oxide hemihydrobromide, a 2:1 adduct of the base α-picoline N-oxide with hydrogen bromide. It had an infra-red spectrum similar to those of Type A acid salts, and Hadzi thus predicted a structure containing a short symmetrical hydrogen bond with the proton bridging the two oxygen atoms. This prediction was subsequently verified in an x-ray diffraction study of the hemihydrobromide by Mills and Speakman,[2] who found a crystallographically symmetrical hydrogen bond, with O ••• O = 2.3 Å. Unfortunately, the quality of the x-ray data was poor, owing to the decomposition of the crystal in the x-ray beam during data collection, and the present work was initiated in the hope that α-picoline N-oxide hemihydrochloride, if it could be prepared, would prove more stable to x-rays than the hemihydrobromide.

Hadzi's method of preparing N-oxide hydrohalides, by bubbling hydrogen chloride gas into a solution of α-picoline N-oxide in ethanol under strictly anhydrous conditions, was tried, but with no success; only the normal 1:1 adduct could be isolated. Different solvents, such

as acetone and methanol, and various mixtures of these solvents, were tried, but again with no success. As a last resort, some base was dissolved in concentrated hydrochloric acid in a base:acid molar ratio of 2:1. Two crystalline products were obtained: one was identified from its infra-red spectrum as the free base, but the other product had an infra-red spectrum which was almost identical to that of α-picoline N-oxide hemihydrobromide, except for an additional peak at 3,300 cm^{-1} due to hydration. A density determination (by flotation) of the latter product implied that the stoichiometry corresponded to the hydrated neutral salt [B.HCl.H_2O], where B = α-picoline N-oxide. The evidence of the infra-red spectrum was, however, confirmed by the subsequent structure analysis, which revealed the presence of the centrosymmetric ions $[B_2H]^+$ and $[HCl_2]^-$.

5.2. Experimental

Preparation

α-Picoline N-oxide hydrochloride monohydrate was prepared by dissolving some α-picoline N-oxide slowly in an equimolar quantity of concentrated hydrochloric acid. The resulting material was recrystallised from water, to give clear plate-shaped crystals of m.p. 41-43°C. The crystals have plate faces (100) and are elongated parallel to b.

Crystal Data

α-Picoline N-oxide hydrochloride monohydrate, $C_6H_{10}NO_2Cl$, M = 163.6. Orthorhombic, $\underline{a}$ = 17.570(9), $\underline{b}$ = 6.793(5), $\underline{c}$ = 13.345(9) Å, $\underline{U}$ = 1591.5 Å^3. $\underline{D}_m$ = 1.35, $\underline{D}_c$ = 1.367, z = 8. Space group (unambiguously from absences) $\underline{Pccn}$ (No. 56). F(ooo) = 688, $\mu(MoK_\alpha)$ = 4.2 cm^{-1}.

5.3.(a) Collection of x-ray data.

A crystal of dimensions 0.45 x 0.35 x 0.15 m.m^3 was mounted along its $\underline{b}$ axis and dipped in a diluted solution of the mounting glue to form a protective coating, since exposure to x-rays caused rapid decomposition. Preliminary crystal data were determined photographically, and more accurate cell dimensions were derived by a least-squares treatment of high-order reflections whose θ values had been measured on a Hilger and Watts four-circle diffractometer, using Mo-K_α (λ = 0.71069 Å).

Intensity data were collected on the diffractometer using filtered Mo radiation, out to $\theta = 20^\circ$. The two standard reflections remained constant throughout the data collection, indicating that the protective coating had successfully prevented decomposition. It was not considered worthwhile collecting data beyond $\theta = 20^\circ$ because of the fairly rapid fall off in scattered intensity with increasing θ. A total of 753 independent intensities were measured, of which 498 with $|F| > 3\sigma(|F|)$ were used in the structure analysis and refinement. Lorentz and

polarisation corrections were applied to the data, but no corrections for absorption were made ($\mu R \sim 1.3$).

5.3.(b) Structure Determination and Refinement (x-ray data)

The structure was solved by the symbolic addition method using versions of the X-RAY 70 programs DATFIX, SIGMA2 and PHASE adapted for use on the Glasgow KDF 9 computer. Normalised structure amplitudes (E 's) were calculated for all the observed structure amplitudes, and the 110 reflections with $E > 1.4$ were used to derive 1148 Σ_2 relationships. An origin was defined by assigning as positive the signs of the reflections 15 2 2, 6 6 1, and 4 1 11; starting with this basic set of signs, the phase-determining procedure yielded the signs of 94 reflections, and an E-map calculated using these phased E's as coefficients revealed all the non-hydrogen atoms. Structure factors calculated using the atomic co-ordinates obtained from the E-map gave an R-factor of 39% which was reduced to 15.5% after four cycles of full-matrix least-squares refinement with isotropic vibrational parameters, and further to 10.1% after four cycles of block-diagonal refinement with anisotropic vibrational parameters. Hydrogen atoms were not included at this stage of the refinement, but a further two cycles of refinement in which hydrogen atoms were included (but not refined) using the co-ordinates obtained from the refinement of the neutron data reduced R to a final value of 7.8%, with R' (= $W\Delta^2 / WFo^2$) at 0.62%. The weighting scheme applied in the final four cycles is

represented by the equation $\sqrt{w} = [1-\exp(-P_1(\sin/\lambda)^2)]/[1+P_2 Fo + P_3 Fo^2 + P_4 Fo^3]^{\frac{1}{2}}$; the final values of P_1, P_2, P_3, and P_4 were 20, 0.0001, 0.0005 and 0.0 respectively. The atomic scattering factors were taken from reference (3). The final x-ray positional and vibrational parameters are given in Tables 5.1(a) and 5.2(a) while Table 5.3. lists the observed structure amplitudes and structure factors calculated from the final least-squares parameters.

5.4.(a) Collection of the neutron data.

Crystals of a size suitable for neutron diffraction were obtained by crystallisation from a saturated solution of α-picoline N-oxide hydrochloride in water over a period of about 5 days. A crystal of dimensions 8 x 6 x 2 mm^3 was selected and mounted along b. Integrated intensities for 1,273 independent reflections were measured on an automatic four-circle diffractometer in the DIDO reactor at A.E.R.E. Harwell, using a neutron beam monochromated to a wavelength of 1.172 Å. The diffracted intensities suffered from a fall-off in magnitude with increasing Bragg angle similar to that found with the x-ray intensities. This was probably due to the high level of incoherent scattering (50% of the nuclei in the crystal are hydrogens) combined with large atomic vibrational effects resulting from a loosely bound lattice; the latter effect would also explain the fall-off in the x-ray intensities. As a result, only 599 reflections had structure amplitudes which were statistically significant ($|F| > 3\sigma(|F|)$). Absorption corrections

were applied to these observed data using a μ(effective) of 1.88 cm^{-1}, the incoherent scattering cross-section of hydrogen being taken as 37×10^{-24} cms.

5.4.(b) Structure Analysis and Refinement (neutron data)

The starting point of the neutron structure analysis was the set of atomic co-ordinates determined for the non-hydrogen atoms during the x-ray analysis. A synthesis of neutron scattering density using the observed neutron structure amplitudes and phases calculated from the x-ray-determined co-ordinates revealed most of the negatively-scattering hydrogen nuclei in their expected positions. One of the two crystallographically distinct water molecules was found to be disordered; the proton which was expected to be at the centre of the bichloride ion also appeared to be disordered, and a difference synthesis with coefficients $[F_{obs} - F_c]$, where F_c was calculated for all atoms except the bichloride ion proton, also showed apparent disorder (Figure 5.1.). To accept this disorder as genuine would imply a Cl-H bond length of about 0.7 Å; since the Cl-H bond length in hydrogen chloride is 1.275 Å a Cl-H bond length of 0.7 Å is clearly unacceptable and the 'disorder' must therefore be a diffraction effect, the neutron data being neither sufficiently accurate or numerous to resolve a small negative peak at a point between two large positive peaks.

The 599 'observed' reflections were used in the refinement of the structure. Two cycles of full-matrix isotropic least-squares analysis

were followed by five cycles of anisotropic, block-diagonal analysis, and the R-factor at convergence was 12.17%, with $R'(\Sigma W\Delta^2/\Sigma F_o^2)$ = 1.76%.

The nuclear scattering-lengths used were 0.661, 0.577, 0.940, 0.990 and -0.378×10^{-12} cm for C, O, N, Cl, and H respectively. Unit weights were used throughout the refinement.

The final neutron positional and vibrational parameters are given in Tables 5.1(b) and 5.2(b), whilst the observed structure amplitudes and calculated structure factors are listed in Table 5.4.

5.5. Description and Discussion of the Structure

Although the x-ray and neutron diffraction analyses of α-picoline-N-oxide hydrochloride monohydrate have not provided particularly accurate bond lengths and angles, they have nevertheless proved worthwhile in revealing an unexpectedly interesting structure.

A density determination had indicated that the stoichiometry of the crystals corresponds to that of a normal hydrated neutral salt $[BH^+Cl^-H_2O]$. The crystal structure analysis, however, has revealed the presence of the two symmetric ions $[B_2H]^+$ (where B = α-picoline N-oxide), and $[HCl_2]^-$. This can be described as a disproportionation, in which a neutral salt has reverted in part to a basic salt $[B_2H]^+$ and in part to an acid salt $[HCl_2]^-$:

$$2[BH^+Cl^-H_2O] \equiv [BHB]^+[ClHCl]^-.2H_2O$$

A view of the structure along the c-axis is given in Figure 5.2. The $[B_2H]^+$ cations are situated on centres of symmetry and form relatively tightly-bound layers in the bc plane at $x \approx 0$ and $x \approx \frac{1}{2}$. The $[HCl_2]^-$ anions are situated on the two-fold axis parallel to c, and are linked together (via hydrogen bonding) by water molecules to form loosely-bound layers in the bc plane at $x \approx \frac{1}{4}$ and $x \approx \frac{3}{4}$ There is no hydrogen-bonding between these alternate layers of anions and cations.

The bond lengths and angles in the α-picoline N-oxide residue from both the x-ray and neutron analyses are listed in Table 5.5., and the numbering system adopted is shown in Figure 5.3. The dimensions determined by the x-ray and neutron analyses do not differ significantly from each other or from their expected values. A comparison of the α-picoline N-oxide bond lengths with those of some other pyridine N-oxides is given in Table 5.6.

The pyridine ring of the α-picoline N-oxide residue is planar within the limits of experimental error. The mean plane through the ring is defined by the equation (based on the x-ray co-ordinates) $-0.1395X + 0.2124Y - 0.9673Z = -4.698$ Å, and the root mean square deviation of the atoms from the plane is 0.008 Å. Atoms O(1) and C(6) are displaced from the plane of the ring by +0.02 Å and +0.03 Å respectively.

The anisotropic temperature factors (neutron analysis) of the methyl group suggest that, although the group is not rotating freely,

it is oscillating about the C(1)-C(6) bond with a root mean square amplitude of about 28°. The orientation of the group with respect to the pyridine ring can be defined by the angles which the three methyl C-H bonds subtend with the plane of the pyridine ring. They are, for C(6)-H(5), C(6)-H(6) and C(6)-H(7) respectively, 55.1°, 1.4° and 62.3°.

The oxygen atom O(1) is involved in a short, crystallographically-symmetric hydrogen bond across the centre of symmetry at 0, $\frac{1}{2}$, 0; the O •••• O distance of 2.421(9) Å compares with a value of 2.418(11) Å for a similar O ••• H ••• O bond in acetamide hemihydrochloride.[4] The proton, H(1), was located by the neutron analysis at the centre of symmetry, as expected, but this is not, in itself, evidence that the proton is situated exactly mid-way between the two centrosymmetrically-related oxygen atoms; two potential-energy minima less than 0.1 Å on either side of the centre would give the same result in a diffraction experiment as a single potential-energy minimum. The arguments as to whether the proton in a very short, crystallographically symmetric hydrogen bond is truly centred have been widely discussed, and the most favoured interpretation of the accumulated spectroscopic and crystallographic evidence is that the proton is situated in a "broad, flat unharmonic potential, possibly with a bump in the middle no more than 200 cm^{-1} in height, but also possibly completely flat."[5]

The bond lengths and angles between the bichloride ion and the (two crystallographically distinct) water molecules are listed in Table

5.7. Figure 5.4. shows the hydrogen-bonded system involving the bichloride ion and water molecules projected along a; the α-picoline N-oxide residues have been omitted for clarity. The oxygen atoms of the water molecules are situated on the two-fold axis at $\frac{1}{4}$, $\frac{1}{4}$, z, while the bichloride ion is situated about the two-fold axis at $\frac{1}{4}$, $\frac{1}{2}$, z. The water molecules act as hydrogen-bonding bridges between the bichloride ions, with the water molecule based on O(3) utilising both of its (crystallographically equivalent) hydrogen atoms for this purpose. The water molecule based on O(2) is disordered about the two-fold axis, using only one of its hydrogen atoms in forming O-H•••Cl bonds (effectively $\frac{1}{2}$H in each bond), the other hydrogen atom being used in forming an O-H•••O hydrogen bond along the two-fold axis between adjacent water molecules, with an O ••• O distance of 2.723(8) Å (as determined from the x-ray analysis). The O(2) ••• Cl and O(3) ••• Cl distances of 2.982(7) Å and 3.062(8) Å respectively (x-ray analysis) are comparable with the average length of O-H•••Cl^- bonds quoted by Pimentel and McClellan[6] of 3.12(13) Å. The standard deviations of the water molecule hydrogen positions (from the neutron analysis) are too large for any meaningful comment to be made about the geometry of the water molecules and their hydrogen bonds.

The most interesting part of the structure is undoubtedly the bichloride ion, $[Cl \cdots H \cdots Cl]^-$. The bichloride ion was first detected in 1958 by Waddington[7] during an infra-red study of $N(CH_3)_4^+HCl_2^-$, and since then has been extensively studied, mainly by infra-red

spectroscopy, by Waddington and Salthouse,[8] Evans and Lo[9] and McDaniel and Vallée.[10] Evans and Lo identified two different types of spectra which they classified as Type I and Type II. Type I spectra they attributed to salts containing a linear but noncentrosymmetric HCl_2^- ion (point group $C_{\infty v}$) while Type II spectra were attributed to salts containing a linear, centrosymmetric HCl_2^- ion (point group $D_{\infty h}$). Later work by Stirling, Ludman and Waddington[11] on the inelastic neutron scattering spectra and Raman spectra of the Type I salts $CsHCl_2$ and $CsDCl_2$ showed that the bichloride ion was bent in these salts, having the point group C_{2v} or C_s, and nuclear quadrupole resonance studies by Smith et al[12] of a series of salts containing HCl_2^- and DCl_2^- ions confirmed Evans and Lo's classification of bichloride ions into two types.

The crystal structures of only two salts containing bichloride ions have been reported; the Type II salt CsCl ($H_3O^+HCl_2^-$) has a Cl ••• Cl distance of 3.14(2) Å,[13] and has a mirror plane perpendicular to the Cl ••• Cl axis, while the Type I salt $Me_4N^+HCl_2^-$ has a Cl ••• Cl distance of 3.22(2) Å and has no mirror plane perpendicular to the Cl ••• Cl axis.[14] The bichloride ion in the present structure has a Cl ••• Cl distance of 2.891(5) Å and a two-fold axis perpendicular to the Cl ••• Cl axis, thus suggesting a Type II structure. The bending and asymmetric stretching modes, ν_2 and ν_3, of the HCl_2^- ion cannot be identified in the infra-red spectrum of α-picoline N-oxide hydrochloride monohydrate because of interference from the cation absorptions. How-

ever, a weak, fairly broad peak which can be assigned to the symmetric stretching frequency, ν_1, is observed centred at 278 cm^{-1} (Figure 5.5.). The symmetric stretching of the cation $[B \cdots H \cdots B]^+$ would also be expected around this region of the spectrum, but since the ion is centrosymmetric, it is infra-red inactive. The value of 278 cm^{-1} for ν_1 can be compared with values of 266 cm^{-1} and 240 cm^{-1} for ν_1 in the Type II salts $(C_3H_7)_4N^+HCl_2^-$ and $(C_5H_{11})_4N^+HCl_2^-$ respectively.[9] The higher frequency of ν_1 in the present structure suggests a stronger Cl ••• H ••• Cl bond; the bond length of 2.891(5) Å is significantly shorter than those of the other two bichloride ions whose dimensions are known, but it is likely that the large thermal vibrations (root mean square amplitude about 0.1 Å) of the chlorine atoms normal to the Cl ••• Cl axis have caused an apparent shortening of the Cl ••• Cl distance. An estimate of the magnitude of this apparent shortening, calculated using Cruickshank's method,[15] is 0.13 Å. This gives a corrected Cl ••• Cl distance of 3.02 Å, still significantly shorter than the Cl ••• Cl distances in $CsCl\frac{1}{2}(H_3O^+HCl_2^-)$ and $(C_2H_5)_4N^+HCl_2^-$.

The shortest intermolecular contacts (those significantly less than the normal van der Waals contact distances for the atoms involved) are listed in Table 5.8.

The methyl groups are related by the two-fold axis, the contact distance being 3.60 Å (x-ray analysis). This is significantly less than twice the accepted van der Waals radius of the methyl group (4.0 Å), but the groups are not rotating freely and are staggered with respect to each other; the hydrogen atoms of one methyl group are thus able to fit

into the spaces between the hydrogen atoms of the symmetrically-related methyl group without involving any very short H ••• H contacts, all of the H ••• H contacts between the methyl groups being greater than twice the van der Waals radius of hydrogen (2.4 Å). The shortest such contact is, in fact, 2.74 Å.

A similar argument applies to the two methyl-chlorine contacts of 3.68 Å and 3.74 Å (x-ray analysis).

More interesting are the contacts involving C(5), H(4) and the bichloride ion. The C(5) ••• Cl distance of 3.50 Å (x-ray analysis) is approximately 0.3 Å shorter than the sum of the carbon and chlorine van der Waals radii, and, more important, the Cl ••• H(4) distance of 2.40 Å is 0.5 Å less than the sum of the hydrogen and chlorine van der Waals radii (using Pauling's value for hydrogen of 1.2 Å). The C - H ••• Cl angle is 155°, and it therefore seems reasonable to conclude that C(5) - H(4) ••• Cl represents a genuine C - H ••• Cl hydrogen bond.

References

1. D.Hadzi, J.Chem.Soc., 988, 5128 (1962).
2. H.H.Mills and J.C.Speakman, Proc.Chem.Soc., 216 (1963).
3. "International Tables for Crystallography", Vol.3, Kynoch Press, Birmingham (1962).
4. S.W.Peterson and J.E.Worsham(jun.), U.S.Atomic Energy Commission, ORNL, 2782, 69 (1959).
5. A.Sequeira, C.A.Berkebile and W.C.Hamilton, J.Mol.Structure, 1, 288 (1967-8).
6. G.C.Pimentel and A.L.McClellan, Ann.Rev.Phys.Chem., 22, 347 (1971).
7. T.C.Waddington, J.Chem.Soc., 1708 (1958).
8. J.A.Salthouse and T.C.Waddington, J.Chem.Soc.A., 28 (1966).
9. J.C.Evans and C.Y-S.Lo, J.Phys.Chem., 70, 11 (1966).
10. D.H.McDaniel and R.E.Vallee, Inorg.Chem., 2, 996 (1963).
11. G.C.Stirling, C.J.Ludman and T.C.Waddington, J.Chem.Phys.,52, 2730 (1970).
12. C.J.Ludman, T.C.Waddington,J.A.Salthouse, R.J.Lynch and J.A.S. Smith, Chem.Comm., 405, (1970).
13. L.W.Schroeder and J.A.Ibers, Inorg.Chem., 7, 594 (1968).
14. J.S.Swanson and J.M.Williams, Inorg. Chem. Letters, 6, 271 (1970).
15. D.W.J.Cruickshank, Acta.Cryst., 9, 747,754 (1956).
16. D.R.Johnson and W.H.Watson, Inorg.Chem., 10(6), 1281 (1971).
17. S.Scavnicar and B.Matkovic, Acta.Cryst., B.25, 2046 (1969).
18. R.S.Sager, R.J.Williams and W.H.Watson, Inorg.Chem., 6, 951 (1967).

TABLES AND DIAGRAMS

Table 5.1

Fractional co-ordinates ($\underline{x}$, $\underline{y}$, $\underline{z}$) and absolute co-ordinates (in Å, with $\underline{X} = a\underline{x}$, $\underline{Y} = b\underline{y}$, $\underline{Z} = c\underline{z}$, and with standard deviations in parentheses.)

(a) X-ray analysis

	$\underline{x}$	$\underline{y}$	$\underline{z}$	$\underline{X}$	$\underline{Y}$	$\underline{Z}$
Cl	0.2073	0.5681	0.3399	3.642(4)	3.857(4)	4.534(4)
N	-0.0122	0.2737	0.3972	-0.215(5)	1.859(7)	5.299(6)
O(1)	-0.0286	0.4632	0.4196	-0.502(6)	3.145(5)	5.597(6)
O(2)	0.2500	0.2500	0.1965	4.393	1.698	2.621(9)
O(3)	0.2500	0.2500	0.4924	4.393	1.698	6.569(10)
C(1)	-0.0696	0.1409	0.3928	-1.223(8)	0.957(8)	5.240(7)
C(2)	-0.0519	-0.0452	0.3682	-0.911(9)	-0.307(9)	4.912(8)
C(3)	0.0234	-0.1023	0.3492	0.410(9)	-0.695(10)	4.659(8)
C(4)	0.0793	0.0375	0.3524	1.393(8)	0.255(9)	4.702(9)
C(5)	0.0618	0.2230	0.3775	1.086(8)	1.514(10)	5.036(8)
C(6)	-0.1485	0.2170	0.4138	-2.609(8)	1.474(12)	5.520(10)

(b) Neutron analysis

Cl	0.2074	0.5628	0.3421	3.645(15)	3.821(13)	4.564(11)
N	-0.0123	0.2736	0.3969	-0.217(7)	1.858(8)	5.294(6)

Table 5.1 (cont'd)

	x	y	z	X	Y	Z
O(1)	-0.0306	0.4601	0.4212	-0.538(20)	3.124(16)	5.616(19)
O(2)	-0.2500	0.2500	0.1955	-4.393	1.698	2.606(20)
O(3)	-0.2500	0.2500	0.4871	-4.393	1.698	6.499(21)
C(1)	-0.0693	0.1465	0.3935	-1.217(9)	0.994(12)	5.249(9)
C(2)	-0.0500	-0.0466	0.3680	-0.877(12)	-0.317(13)	4.910(10)
C(3)	0.0243	-0.1020	0.3488	0.427(12)	-0.693(12)	4.653(10)
C(4)	0.0811	0.0402	0.3522	1.424(9)	0.273(14)	4.699(12)
C(5)	0.0605	0.2263	0.3758	1.064(11)	1.537(13)	5.015(11)
C(6)	-0.1477	0.2136	0.4139	-2.595(11)	1.451(16)	5.520(12)
H(1)	-0.0973	-0.1590	0.3656	-1.710(3)	-1.08(3)	4.88(4)
H(2)	0.0335	-0.2548	0.3311	0.59(3)	-1.73(3)	4.41(3)
H(3)	0.1365	-0.0022	0.3351	2.40(3)	-0.02(4)	4.47(3)
H(4)	0.1002	0.3596	0.3847	1.76(2)	2.44(3)	5.13(3)
H(5)	-0.1529	0.2847	0.4828	-2.69(3)	1.93(7)	6.44(4)
H(6)	-0.1815	0.0943	0.4071	-3.26(4)	0.64(5)	5.43(6)
H(7)	-0.1666	0.3196	0.3619	-2.93(3)	2.17(5)	4.82(4)
H(8)	0.2403	0.3610	0.2424	4.22(6)	2.45(6)	3.23(5)
H(9)	0.2500	0.2500	0.1203	4.39	1.70	1.60(10)
H(10)	0.2377	0.3495	0.4584	4.18(5)	2.37(4)	6.11(3)
H(11)	0.2319	0.6442	0.3518	4.08(3)	4.38(4)	4.69(3)
H(12)	0.0000	0.5000	0.5000	0.00	3.40	6.67

Table 5.2

Vibrational parameters ($Å^2$) with standard deviations in parentheses.

(a) X-ray analysis

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Cl	0.105(2)	0.096(2)	0.114(3)	-0.018(4)	0.005(4)	0.001(4)
N	0.059(4)	0.041(4)	0.038(3)	-0.015(7)	-0.011(7)	0.003(7)
O(1)	0.084(4)	0.038(3)	0.075(4)	-0.024(6)	-0.036(7)	-0.014(6)
O(2)	0.153(10)	0.112(9)	0.048(5)	0.000	0.000	-0.094(17)
O(3)	0.167(11)	0.102(8)	0.063(6)	0.000	0.000	-0.029(18)
C(1)	0.054(5)	0.038(4)	0.035(4)	-0.015(8)	-0.005(8)	-0.031(8)
C(2)	0.057(6)	0.050(5)	0.051(5)	-0.019(9)	0.005(9)	-0.045(9)
C(3)	0.074(6)	0.059(6)	0.042(5)	-0.002(10)	-0.005(9)	0.019(11)
C(4)	0.045(5)	0.058(6)	0.065(6)	-0.021(10)	-0.001(9)	0.005(9)
C(5)	0.041(5)	0.066(6)	0.052(5)	0.029(10)	-0.001(9)	-0.039(10)
C(6)	0.032(4)	0.098(8)	0.075(6)	-0.021(12)	0.021(9)	0.016(11)

(b) Neutron analysis

Cl	0.156(12)	0.070(8)	0.077(6)	-0.015(12)	0.063(14)	0.041(16)
N	0.054(4)	0.024(4)	0.043(3)	-0.016(7)	-0.004(6)	-0.005(7)
O(1)	0.113(15)	0.039(9)	0.088(11)	-0.004(17)	-0.063(21)	-0.006(20)
O(2)	0.156(30)	0.057(18)	0.051(10)	0.000	0.000	0.107(41)
O(3)	0.148(26)	0.063(18)	0.045(9)	0.000	0.000	-0.023(39)
C(1)	0.039(5)	0.038(6)	0.038(4)	0.001(10)	0.004(8)	-0.012(10)

Table 5.2(b) (cont'd)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
C(2)	0.073(7)	0.034(7)	0.038(4)	-0.007(11)	-0.001(10)	-0.089(13)
C(3)	0.056(6)	0.041(7)	0.050(5)	-0.008(11)	0.005(11)	0.007(12)
C(4)	0.026	0.058(8)	0.060(6)	0.010(12)	-0.017(8)	0.002(11)
C(5)	0.056(6)	0.029(7)	0.060(6)	-0.015(12)	0.011(11)	-0.048(11)
C(6)	0.042(5)	0.087(11)	0.061(17)	-0.021(15)	0.019(10)	-0.018(13)
H(1)	0.089(18)	0.094(25)	0.137(26)	-0.058(45)	0.056(37)	-0.144(39)
H(2)	0.102(19)	0.067(18)	0.104(18)	-0.037(36)	0.009(32)	0.026(33)
H(3)	0.085(19)	0.181(33)	0.027(9)	-0.039(30)	-0.048(22)	0.027(39)
H(4)	0.056(12)	0.098(22)	0.135(21)	-0.034(40)	-0.034(29)	-0.163(30)
H(5)	0.087(21)	0.254(58)	0.130(26)	-0.166(74)	-0.006(42)	0.137(65)
H(6)	0.112(25)	0.113(39)	0.255(51)	-0.006(81)	0.002(65)	-0.111(56)
H(7)	0.111(23)	0.238(57)	0.118(26)	0.166(67)	0.049(42)	0.216(65)
H(8)	0.115(40)	0.067(38)	0.071(24)	0.011(58)	-0.095(55)	-0.058(73)
H(9)	0.121(29)	0.039(22)	0.296(96)	0.000	0.000	0.048(48)
H(10)	0.174(33)	0.108(28)	0.078(17)	-0.085(35)	0.073(45)	-0.096(61)
H(11)	0.039(21)	0.050(28)	0.061(19)	-0.147(42)	0.000(29)	-0.120(42)
H(12)	0.098(30)	0.031(20)	0.082(20)	0.000(33)	-0.020(43)	-0.011(36)

Table 5.3

Observed structure amplitudes and final calculated structure factors (x-ray analysis).

H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC
16	2	0	16.7	-18.2	10	3	1	12.2	8.7	8	0	6	20.9	-18.5	5	5	1	13.3	13.5	3	6	3	18.4	19.9	2	1	3	9.1	11.1
16	1	2	9.8	9.4	8	0	4	56.4	54.8	5	5	0	18.2	-17.2	3	6	1	14.3	14.8	2	1	2	103.2	103.4
15	2	3	9.4	-11.0	8	0	2	24.0	23.4	5	4	8	6.5	-4.7	3	5	6	8.9	-10.1	2	1	1	25.2	32.3
15	2	2	28.7	28.7	10	2	6	13.9	13.1	8	0	0	37.1	-37.2	5	4	6	8.8	-9.4	3	5	5	12.2	-12.8	2	0	12	10.4	-8.9
15	2	1	15.5	-15.1	10	2	5	14.8	-14.1	7	5	3	21.0	-19.1	5	4	5	16.5	17.4	3	5	4	29.9	29.7	2	0	10	7.2	6.3
15	1	5	10.2	10.1	10	2	1	12.1	11.2	7	5	1	14.6	13.8	5	4	4	6.7	5.9	3	5	3	18.7	-16.5	2	0	8	37.1	39.3
15	1	4	16.1	-17.5	10	2	0	29.7	28.9	7	5	0	16.3	16.7	5	4	1	17.2	-18.8	3	5	2	10.8	11.5	2	0	6	94.5	-89.8
15	1	0	28.8	30.8	10	1	9	9.6	11.9	7	4	7	20.5	18.3	5	3	10	6.0	7.4	3	5	1	23.9	24.0	2	0	4	143.3	-125.5
15	0	4	25.7	-26.6	10	1	7	13.9	13.6	7	4	5	11.5	-9.9	5	3	9	13.0	-14.7	3	5	0	21.4	-22.8	1	6	5	9.2	9.9
14	3	2	16.6	-11.9	10	1	5	15.8	-17.0	7	4	4	7.3	-7.9	5	3	8	5.7	-4.5	3	4	9	9.0	9.0	1	6	4	7.3	5.6
14	3	1	7.3	-7.7	10	1	3	21.4	-20.5	7	4	2	16.2	-15.3	5	3	7	6.0	7.9	3	4	7	10.5	11.0	1	6	3	18.1	18.6
14	2	6	19.1	19.7	10	1	2	19.6	-19.8	7	4	1	13.8	15.0	5	3	5	7.0	5.2	3	4	6	6.8	-6.8	1	6	2	10.9	-10.4
14	2	5	9.7	9.5	10	0	10	9.8	-8.9	7	3	10	13.8	-13.3	5	3	4	5.9	-8.4	3	4	5	23.9	-21.0	1	5	8	7.2	-7.4
14	2	2	11.9	-11.9	10	0	8	6.5	-6.9	7	3	9	8.5	-10.2	5	3	3	14.6	-13.0	3	4	4	14.9	-12.1	1	5	5	11.2	-9.8
14	1	6	12.2	-11.7	10	0	6	22.5	21.7	7	3	5	9.1	8.5	5	3	2	13.7	11.9	3	4	3	10.8	11.6	1	5	2	6.4	-5.5
14	1	5	16.0	17.6	10	0	4	6.2	-4.5	7	3	4	16.8	-16.0	5	3	1	13.0	11.1	3	4	2	16.9	16.0	1	5	1	11.4	10.8
14	1	4	12.0	9.1	10	0	2	24.4	-23.8	7	3	0	11.5	11.3	5	3	0	63.6	61.5	3	4	1	31.3	31.0	1	4	10	7.8	7.5
14	1	3	9.5	-12.7	10	0	0	16.3	-13.9	7	2	9	6.1	6.3	5	2	11	9.0	6.3	3	3	8	5.7	2.2	1	4	7	10.7	-10.5
14	1	2	18.6	21.7	9	5	4	10.0	-11.1	7	2	5	40.2	-41.6	5	2	8	8.8	9.8	3	3	7	5.7	-7.9	1	4	6	9.3	-8.7
14	1	1	22.4	-23.2	9	5	2	9.4	9.6	7	2	3	25.5	24.8	5	2	7	25.9	-25.5	3	3	6	39.4	-40.0	1	4	4	7.6	8.0
14	0	4	26.7	-28.0	9	5	1	6.6	7.7	7	2	2	24.6	-23.2	5	2	6	14.1	13.4	3	3	3	10.2	9.2	1	4	3	29.8	25.6
14	0	0	35.8	33.5	9	5	0	11.0	12.8	7	2	1	58.7	61.5	5	2	5	8.2	12.5	3	3	2	17.5	20.2	1	4	1	15.8	11.8
13	4	2	13.5	-14.0	9	4	7	7.4	6.7	7	1	9	24.8	24.1	5	2	4	47.9	-46.6	3	3	0	55.8	-58.3	1	3	11	7.6	8.4
13	3	5	6.9	-6.6	9	4	6	11.4	11.1	7	1	8	7.8	7.2	5	2	3	30.0	28.3	3	2	11	13.3	-12.8	1	3	8	8.7	-3.5
13	3	4	12.9	11.8	9	4	5	14.3	14.4	7	1	5	37.4	-36.7	5	2	2	41.6	-34.3	3	2	7	7.0	9.0	1	3	7	18.6	-17.2
13	3	0	15.0	-11.5	9	4	4	7.8	-8.8	7	1	3	14.0	19.1	5	2	1	5.0	-6.9	3	2	5	32.2	-34.2	1	3	6	38.9	39.6
13	2	7	6.7	7.4	9	4	3	18.3	-18.5	7	1	2	29.8	-31.3	5	1	10	6.8	-7.9	3	2	4	25.5	24.0	1	3	5	20.7	-21.0
13	2	6	16.9	-12.9	9	4	2	5.9	5.6	7	1	1	14.4	8.5	5	1	9	9.1	-9.5	3	2	3	39.9	37.1	1	3	2	16.5	-20.6
13	2	4	6.9	-1.0	9	4	1	24.0	-22.7	7	1	1	22.1	22.9	5	1	7	15.3	15.5	3	2	2	56.8	-53.7	1	3	1	30.9	28.5
13	2	3	13.4	-15.0	9	3	9	8.8	-8.2	7	0	8	9.4	10.8	5	1	6	10.7	-10.7	3	2	1	70.6	76.3	1	3	0	69.5	78.9
13	2	1	11.3	-12.2	9	3	7	7.8	9.4	7	0	6	9.4	10.8	5	1	5	13.8	-10.7	3	1	11	10.2	13.8	1	2	11	7.9	-8.1
13	1	4	11.5	-13.6	9	3	5	10.1	9.3	7	0	4	70.3	-66.0	5	1	4	10.7	-13.2	3	1	10	25.2	24.8	1	2	10	13.1	-13.9
13	1	3	9.3	10.9	9	3	4	14.4	15.5	7	0	2	29.2	-25.2	5	1	3	72.8	-76.9	3	1	9	16.9	14.8	1	2	9	6.1	4.1
13	1	1	15.6	-16.2	9	3	3	6.6	-4.7	6	6	1	21.9	23.7	5	1	2	14.8	-15.9	3	1	8	9.6	-9.1	1	2	8	7.1	8.3
13	0	4	6.4	4.5	9	3	0	9.8	-9.1	6	6	0	9.1	-8.1	5	1	1	85.5	85.8	3	1	7	57.0	-56.1	1	2	7	5.1	3.3
13	0	2	21.2	-19.5	9	2	8	18.4	-16.2	6	5	5	5.5	1.7	5	0	12	10.0	-11.9	3	1	6	13.4	-15.9	1	2	4	48.4	-48.0
12	4	3	7.5	4.9	9	2	7	15.0	-16.9	6	5	4	12.0	12.0	5	0	8	36.2	36.5	3	1	5	32.6	-32.1	1	2	3	10.6	8.8
12	3	6	7.7	-7.0	9	2	5	8.5	8.1	6	5	3	11.3	-12.1	5	0	6	10.5	-10.3	3	1	4	42.1	41.7	1	2	2	76.6	76.3
12	3	4	20.3	-21.3	9	2	4	8.2	7.8	6	5	2	14.8	16.1	5	0	4	17.7	-22.3	3	1	3	94.4	94.9	1	1	12	10.6	9.5
12	3	2	20.4	19.6	9	2	3	15.0	13.9	6	5	1	15.0	-14.4	5	0	2	6.9	10.5	3	1	2	32.5	35.6	1	1	11	18.5	19.6
12	2	7	12.4	-13.5	9	2	2	15.6	-15.5	6	4	9	11.5	-8.0	4	6	4	11.6	8.7	3	0	12	8.6	-7.9	1	1	10	8.3	-10.1
12	2	5	6.6	-9.3	9	1	7	19.3	18.8	6	4	7	6.0	-1.7	4	6	3	11.6	-11.5	3	0	10	7.4	7.5	1	1	9	8.8	-9.0
12	2	4	13.9	12.0	9	1	6	19.7	-21.7	6	4	7	7.3	6.1	4	6	1	21.4	23.0	3	0	8	8.0	6.7	1	1	7	56.6	-53.3
12	2	3	7.3	6.6	9	1	5	12.5	-11.6	6	4	6	27.5	-27.8	4	6	0	21.3	-18.6	3	0	6	13.9	14.3	1	1	6	25.1	-18.6
12	2	1	7.3	6.9	9	1	4	25.3	-23.6	6	4	4	10.2	-10.0	4	5	7	14.5	15.4	2	6	3	13.9	-15.5	1	1	4	54.0	-56.8
12	2	0	33.6	-32.4	9	1	3	41.0	-42.3	6	4	3	23.5	-23.9	4	5	5	6.1	-7.6	2	6	1	13.9	16.5	1	1	3	44.6	70.9
12	1	7	9.0	10.2	9	1	2	13.0	12.3	6	4	2	13.3	12.3	4	5	4	22.4	21.6	2	5	5	8.7	6.8	1	1	2	5.5	-5.4
12	1	6	12.5	-13.9	9	1	1	39.4	38.7	6	4	1	23.3	24.4	4	5	3	14.3	-14.2	2	5	2	32.5	31.4	1	1	1	25.3	-20.1
12	1	3	19.8	-21.3	9	1	0	19.8	13.2	6	3	9	9.4	11.2	4	4	9	8.4	6.9	2	5	1	9.5	-9.3	1	0	12	13.9	-13.0
12	1	2	25.8	24.9	9	0	10	14.4	12.6	6	3	6	7.9	7.4	4	4	6	14.1	-13.4	2	4	9	7.3	-5.7	1	0	10	5.6	-1.1
12	1	1	14.9	-14.9	9	0	6	7.1	6.8	6	3	5	24.2	-23.4	4	4	5	14.4	-14.3	2	4	7	6.5	4.3	1	0	8	65.1	64.9
12	0	8	9.1	8.5	9	0	2	76.9	-78.2	6	3	4	8.5	7.7	4	4	3	17.0	15.6	2	4	6	20.2	-19.4	1	0	4	22.1	-22.5
12	0	6	12.7	-12.4	8	5	5	8.4	-9.0	6	3	2	37.1	-34.3	4	4	2	13.9	13.4	2	4	5	8.5	-6.5	1	0	4	73.3	-66.5
12	0	2	10.4	9.4	8	5	2	18.5	17.6	6	3	1	19.0	16.5	4	4	0	29.2	22.7	2	4	4	24.9	-22.8	0	6	4	11.3	7.9
12	0	0	8.6	-7.0	8	5	1	10.9	9.1	6	2	10	6.4	5.4	4	3	8	15.1	-19.3	2	4	3	25.7	-24.4	0	6	0	18.8	-22.5
11	4	3	10.9	-11.4	8	4	7	17.3	-17.9	6	2	9	11.1	-9.9	4	3	6	29.6	28.6	2	4	2	6.7	6.1	0	5	5	15.1	-12.4
11	4	2	24.6	-23.2	8	4	6	10.6	-12.0	6	2	8	6.7	-4.8	4	3	4	18.2	19.7	2	4	1	31.1	30.1	0	5	4	30.3	29.0
11	4	1	12.2	-12.3	8	4	5	12.1	-13.5	6	2	7	6.0	5.1	4	3	3	15.3	-14.6	2	4	0	10.0	16.6	0	4	10	13.1	12.2
11	3	6	17.3	15.8	8	4	3	24.5	24.7	6	2	6	13.0	11.6	4	3	2	32.9	-35.6	2	3	10	18.7	-17.5	0	4	8	6.1	5.1
11	3	4	10.1	-10.4	8	4	0	12.9	12.6	6	2	5	29.5	29.2	4	3	1	22.4	-19.3	2	3	9	6.6	9.9	0	4	6	13.1	-13.2
11	3	2	6.6	-9.3	8	3	9	9.9	11.3	6	2	3	25.2	-31.5	4	2	10	14.9	-15.3	2	3	8	15.3	16.3	0	4	4	14.7	-11.8
11	3	1	6.9	-5.2	8	3	8	10.4	9.5	6	2	2	30.8	32.9	4	2	9	6.2	6.3	2	3	7	10.1	9.4	0	4	2	16.0	18.6
11	3	0	19.7	18.2	8	3	5	14.0	-13.4	6	1	10	9.9	-11.9	4	2	8	11.1	-11.2	2	3	6	21.0	17.9	0	4	0	43.4	49.0
11	2	8	10.7	10.1	8	3	4	23.8	-22.3	6	1	9	16.6	17.5	4	2	7	14.1	-15.5	2	3	5	9.0	-9.6	0	3	9	23.3	-22.0
11	2	6	12.1	-13.9	8	2	9	17.9	16.6	6	1	8	24.3	-24.0	4	2	6	15.9	-15.1	2	3	3	23.6	-23.1	0	3	8	46.4	45.1
11	2	4	13.5	-13.9	8	2	7	20.6	-20.5	6	1	7	12.4	12.9	4	2	5	11.6	-12.1	2	3	2	12.5	4.3	0	3	4	20.5	25.6
11	2	3	2.5	-2.7	8	2	6	13.8	-12.6	6	1	6	14.6	14.0	4	2	4	24.7	-23.7	2	3	1	13.5	-11.1	0	3	2	85.6	-86.1
11	2	2	13.0	10.8	8	2	5	15.7	-15.5	6	1	5	53.1	-53.0	4	2	3	34.9	39.6	2	2	11	8.2	-7.1	0	2	12	9.7	8.5
11	1	9	6.4	6.9	8	2	4	12.4	12.4	6	1	4	13.7	11.9	4	2	2	9.6	7.1	2	2	9	13.8	-13.7	0	2	10	44.5	-45.9
11	1	8	7.1	5.0	8	2	3	32.0	34.3	6	1	3	11.6	-10.9	4	1	12	8.8	9.2	2	2	8	12.5	-11.5	0	2	8	13.3	-13.5
11	1	6	17.5	17.3	8	2	1	6.2	-8.7	6	1	2	13.7	12.6	4	1	11	26.7	26.1	2	2	7	18.2	18.5	0	2	6	36.7	38.8
11	1	4	13.2	-14.1	8	2	0	54.8	-54.1	6	1	1	41.1	45.9	4	1	10	7.9	9.1	2	2	5	15.5	16.7	0	2	4	38.5	-40.9
11	1	2	10.1	-9.0	8	1	11	10.2	10.5	6	0	12	13.0	14.5	4	1	9	13.9	-13.4	2	2	4	42.8	41.9	0	2	2	40.8	-42.1
11	1	0	30.2	37.1	8	1	10	8.1	-8.3	6	0	8	19.6	-19.7	4	1	7	33.0	-32.7	2	2	3	29.7	-32.8	0	1	12	17.9	20.6
11	0	8	17.0	14.4	8	1	7	8.4	-8.2	6	0	6	41.2	-40.5	4	1	6	11.2	-8.4	2	2	2	24.8	31.2	0	1	10	16.4	15.5
11	0	4	31.2	-31.8	8	1	6	8.1	6.8	6	0	4	7.9	-6.8	4	1	4	48.2	46.4	2	2	1	10.0	11.4	0	1	8	52.1	-52.6
11	0	2	23.7	22.9	8	1	5	10.5	11.0	6	0	2	24.8	22.4	4	1	3	22.3	-23.2	2	1	12	14.9	16.6	0	1	6	49.2	-46.8
10	4	6	6.2	-5.5	8	1	4	16.2	14.9	6	0	0	26.0	-24.0	4	1	2	45.3	-39.4	2	1	11	6.9	5.8	0	1	4	137.6	135.3
10	4	5	13.2	-11.9	8	1	3	26.4	-25.5	5	6	3	8.9	9.1	4	1	1	79.0	-65.4	2	1	8	30.0	-29.5	0	0	12	13.5	13.8
10	3	8	6.6	-3.0	8	1	2	9.1	-8.0	5	6	2	10.1	-7.9	4	0	12	6.2	5.2	2	1	7	6.1	-4.2	0	0	8	36.7	35.2
10	3	5	13.3	-12.1	8	1	1	43.5	-43.5	5	5	6	8.0	-7.7	4	0	10	8.4	8.9	2	1	4	20.1	-23.1	0	0	6	33.2	37.7
10	3	4	14.3	13.4	8	0	10	16.0	16.6	5	5	5	14.0	-13.5	4	0	8	26.3	26.3	2	1	3	17.8	-19.9	0	0	4	242.9	-259.7
10	3	2	12.0	-9.1	8	0	8	18.8	-19.3	5	5	4	11.9	12.5	4	0	6	149.0	169.4	2	1	2	6.8	-11.0	0	0	2	15.9	4.0

Table 5.4

Observed structure amplitudes and final calculated structure factors (neutron analysis).

H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc
0	0	4	26.0	-27.3	2	2	8	5.5	-5.2	4	1	1	6.6	-7.4	6	0	0	3.0	-2.7
0	0	6	6.6	-6.0	2	2	9	2.5	-2.1	4	1	2	1.9	1.6	6	0	4	2.6	-1.6
0	0	8	8.0	7.9	2	2	10	2.5	-3.6	4	1	4	3.0	2.8	6	0	6	11.4	-11.5
0	0	10	5.4	5.9	2	3	2	8.8	-7.7	4	1	5	6.6	6.9	6	0	8	5.6	-5.0
0	1	2	14.8	14.3	2	3	3	2.2	-2.2	4	1	6	3.7	-3.2	6	0	12	3.1	3.2
0	1	4	9.6	9.6	2	3	4	4.3	4.1	4	1	7	6.1	-6.3	6	1	2	3.0	-2.9
0	1	6	11.8	-11.4	2	3	5	5.3	-5.3	4	1	8	2.9	-3.4	6	1	3	1.8	-1.6
0	1	8	12.2	-12.9	2	3	6	7.6	7.6	4	1	9	2.7	-1.8	6	1	4	5.7	5.0
0	1	12	6.2	6.9	2	3	8	2.8	1.8	4	1	10	2.0	2.7	6	1	5	5.5	-5.7
0	1	10	2.2	1.6	2	3	9	4.0	3.5	4	1	11	6.8	7.0	6	1	6	4.2	4.5
0	2	0	2.0	2.6	2	3	10	3.5	-4.9	4	1	12	3.0	4.3	6	1	7	2.0	-2.2
0	2	2	6.4	-6.6	2	4	1	8.0	8.0	4	2	1	2.2	-1.3	6	1	8	8.0	-7.6
0	2	4	3.1	-2.9	2	4	3	5.3	-5.6	4	2	2	4.1	-3.4	6	1	9	3.2	3.2
0	2	6	12.5	12.5	2	4	4	7.0	-7.0	4	2	3	2.4	1.9	6	1	10	4.5	-4.5
0	2	8	2.2	-1.4	2	4	5	2.4	-2.7	4	2	4	3.8	-3.8	6	2	0	7.3	-7.3
0	2	10	14.8	-14.7	2	4	6	6.8	-6.5	4	2	8	6.0	-5.6	6	2	1	4.6	5.5
0	3	2	21.1	-22.1	2	4	7	2.1	2.4	4	2	10	7.0	-6.6	6	2	4	7.9	8.0
0	3	6	11.5	11.5	2	4	8	2.1	1.6	4	3	2	11.0	-11.0	6	2	5	1.9	-1.5
0	3	10	2.5	-2.2	2	5	2	8.0	8.0	4	3	4	3.3	3.3	6	2	6	4.0	4.3
0	4	0	12.1	13.3	2	5	4	2.3	-2.7	4	3	6	7.4	7.3	6	2	8	2.2	-2.3
0	4	2	3.7	3.2	2	5	6	2.2	-1.5	4	3	8	2.1	-2.1	6	2	9	2.2	-0.9
0	4	4	7.5	-7.0	3	0	2	6.8	-7.8	4	3	8	5.0	-5.4	6	3	1	2.2	3.0
0	4	6	7.9	-7.2	3	0	4	7.1	-5.9	4	3	10	2.3	-2.4	6	3	2	8.9	-9.0
0	4	8	4.0	3.8	3	0	6	3.1	3.5	4	4	2	2.3	2.2	6	3	5	2.7	-2.8
0	4	10	2.9	1.9	3	0	8	7.6	7.1	4	4	3	2.1	1.2	6	3	6	3.4	2.9
0	5	2	4.1	3.8	3	0	12	4.3	-4.5	4	4	4	2.7	1.9	6	3	8	2.4	2.9
0	5	4	6.5	7.4	3	1	0	4.0	3.8	4	4	5	2.7	-2.6	6	3	9	3.5	3.6
1	0	4	5.8	-7.1	3	1	1	4.9	-5.2	4	4	6	5.4	-5.3	6	4	0	3.1	-4.8
1	0	6	4.5	-4.7	3	1	2	3.2	2.8	4	4	9	2.0	2.2	6	4	1	4.1	3.8
1	0	8	9.8	8.9	3	1	3	10.1	11.1	4	5	2	3.3	2.8	6	4	2	3.3	3.1
1	0	10	2.7	3.5	3	1	4	3.3	-2.3	4	5	3	6.0	-5.4	6	4	3	5.3	-4.9
1	0	12	3.8	-3.6	3	1	5	4.2	-4.6	4	5	4	6.1	6.5	6	4	4	2.5	-2.7
1	1	1	7.7	-7.1	3	1	4	3.3	-2.3	4	5	5	2.2	-1.6	6	4	6	11.1	-11.2
1	1	3	9.0	7.8	3	1	5	4.2	-4.6	4	5	7	4.4	4.6	6	4	7	2.9	2.8
1	1	7	12.4	-11.2	3	1	6	3.5	-4.0	5	0	2	3.4	-2.4	6	4	8	3.1	-2.0
1	1	11	5.4	5.8	3	1	7	11.2	-11.2	5	0	4	5.0	-4.8	6	4	9	2.2	-1.5
1	2	2	4.3	4.9	3	1	9	3.4	3.8	5	0	8	4.8	4.5	6	5	1	3.0	-2.6
1	2	3	2.7	-2.6	3	1	10	7.2	7.4	5	0	12	5.1	-4.9	6	5	2	5.3	4.9
1	2	7	2.6	2.9	3	1	11	2.6	2.1	5	1	1	7.1	7.2	6	5	3	3.5	-2.8
1	2	10	4.3	-4.1	3	1	12	1.9	2.4	5	1	2	2.7	2.9	6	5	4	2.7	2.3
1	2	11	2.7	-3.0	3	2	1	11.2	10.7	5	1	3	6.4	-7.2	6	5	6	2.2	-3.0
1	3	0	5.9	6.9	3	2	2	3.4	-3.7	5	1	4	2.4	1.8	7	0	2	1.9	-1.7
1	3	1	3.9	3.8	3	2	3	6.9	6.7	5	1	5	7.1	-5.9	7	0	4	5.1	-5.2
1	3	2	3.0	-2.9	3	2	4	2.1	2.7	5	1	6	2.7	-2.2	7	0	6	2.1	2.7
1	3	4	2.9	2.4	3	2	5	5.6	-6.2	5	1	7	1.9	0.8	7	0	8	5.3	5.6
1	3	5	4.8	-4.5	3	2	9	3.1	3.2	5	1	8	2.1	1.8	7	0	10	2.0	-1.2
1	3	6	7.5	7.8	3	2	10	2.4	-1.7	5	2	1	9.3	9.0	7	1	0	4.2	-3.7
1	3	7	4.3	-4.4	3	2	11	2.8	-2.9	5	2	2	2.7	-3.9	7	1	1	5.2	3.8
1	3	11	2.2	2.5	3	3	0	2.6	-2.6	5	2	3	11.5	11.0	7	1	3	6.1	-5.6
1	4	1	5.9	5.1	3	3	1	5.8	-5.6	5	2	4	9.9	-9.7	7	1	4	2.7	2.1
1	4	3	7.1	7.0	3	3	2	1.8	1.6	5	2	5	6.3	-6.1	7	1	5	6.6	-6.2
1	4	4	2.6	2.4	3	3	4	2.7	-2.7	5	2	6	3.9	4.5	7	1	8	2.8	-2.9
1	4	6	2.7	-2.2	3	3	6	3.9	-3.8	5	2	7	6.5	-6.8	7	1	9	3.3	2.7
1	4	8	2.8	2.3	3	3	7	3.2	-3.0	5	2	8	5.6	5.3	7	1	10	3.4	3.6
1	4	10	2.3	3.3	3	4	1	3.4	3.1	5	2	10	3.4	-3.7	7	1	11	2.1	-1.4
1	5	0	3.5	-4.0	3	4	5	5.3	-5.3	5	3	0	9.8	10.5	7	2	1	9.2	8.7
1	5	1	2.2	1.7	3	4	6	2.8	-2.3	5	3	1	2.4	-1.0	7	2	3	5.2	4.9
1	5	3	3.3	-3.4	3	4	7	3.3	3.5	5	3	3	3.9	-4.7	7	2	5	6.5	-6.3
1	5	5	3.7	-2.9	3	4	8	4.3	-4.6	5	3	4	2.8	-2.5	7	2	7	2.8	-3.1
1	5	8	2.2	-2.6	3	4	9	2.4	3.6	5	3	5	2.3	2.5	7	2	11	2.6	1.2
2	0	2	3.8	5.3	3	5	0	11.1	-11.5	5	3	6	2.0	-1.2	7	3	0	2.5	2.1
2	0	4	21.6	-20.5	3	5	1	6.6	6.7	5	3	7	3.1	3.7	7	3	2	2.8	-2.5
2	0	6	11.9	-11.5	3	5	2	3.7	3.0	5	3	8	3.1	-2.3	7	3	3	3.0	-2.7
2	0	8	10.9	10.7	3	5	3	5.8	-5.9	5	3	9	6.7	-6.4	7	3	4	2.8	-2.3
2	0	12	5.0	-4.3	3	5	4	14.3	15.1	5	4	1	3.7	-3.4	7	3	5	3.1	3.0
2	1	2	15.5	15.6	3	5	5	6.2	-5.9	5	4	2	3.8	3.7	7	3	6	4.9	5.4
2	1	4	3.4	2.4	3	5	6	4.1	-4.1	5	4	3	2.7	-3.4	7	3	8	2.0	-1.9
2	1	6	4.9	-4.4	3	5	7	2.4	0.3	5	4	4	4.5	4.3	7	3	9	5.1	-5.5
2	1	8	6.0	-5.5	3	5	8	7.4	-7.5	5	4	5	2.9	2.3	7	3	10	4.1	-5.2
2	1	12	7.0	6.3	4	0	0	14.0	16.4	5	4	6	4.1	-4.2	7	4	1	2.2	1.3
2	2	2	2.9	-2.5	4	0	4	12.7	-12.0	5	4	7	2.8	3.1	7	4	2	6.7	-7.1
2	2	4	3.0	3.5	4	0	6	4.6	5.2	5	4	9	2.2	0.5	7	4	3	2.5	-1.7
2	2	5	2.1	1.5	4	0	8	5.0	4.5	5	5	0	8.5	-9.6	7	4	4	3.8	-2.4
2	2	6	4.5	3.3	4	0	10	1.9	2.1	5	5	1	3.3	3.9	7	4	7	6.3	6.4
2	2	7	2.1	1.8	4	0	12	1.8	0.7	5	5	3	3.9	-4.3	7	4	8	2.2	-1.2

Table 5.4 (cont'd).

H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc
7	5	0	3.6	3.6	10	1	7	3.6	2.9	13	3	5	2.3	-2.4	11	1-14		2.0	1.1
7	5	1	2.5	2.7	10	1	9	2.2	1.8	13	4	2	4.3	-3.4	11	3-14		2.0	3.2
7	5	3	6.9	-6.8	10	2	2	3.1	-2.6	14	0	0	12.2	11.4	11	3-13		2.3	-2.3
7	5	4	2.5	1.9	10	2	3	2.2	2.7	14	0	4	10.7	-10.4	12	2-15		2.2	-1.6
7	5	6	2.3	-3.1	10	2	4	3.1	-2.9	14	0	6	3.9	-4.9	12	3-12		2.2	3.5
8	0	0	10.7	-10.9	10	2	5	4.7	-4.3	14	1	1	7.6	-7.8	12	4-13		2.1	-0.8
8	0	2	2.1	2.9	10	2	7	3.8	-3.9	14	1	2	9.7	9.7	13	0-14		2.3	-1.6
8	0	4	7.5	7.2	10	2	9	4.1	4.1	14	1	3	3.4	-3.7	13	0-12		2.9	3.4
8	0	6	6.5	-6.5	10	3	1	6.1	6.0	14	1	4	3.9	3.8	15	0-12		4.2	4.4
8	0	8	6.6	-6.1	10	3	2	2.4	1.8	0	0-16		3.4	-1.3	15	0 -8		8.7	-8.6
8	0	10	5.8	5.5	10	3	3	2.9	2.8	0	1-16		3.5	2.6	15	0 -4		7.1	7.0
8	1	1	2.9	2.1	10	3	5	4.5	-4.9	0	1-14		2.4	-2.8	15	1-10		3.1	3.0
8	1	4	2.7	2.4	10	3	6	3.3	-2.8	0	1-12		6.1	-6.9	15	1 -7		2.6	1.7
8	1	5	2.2	-2.4	10	4	1	3.0	-3.0	0	2-18		3.0	-2.4	15	1 -6		3.6	-3.9
8	1	6	1.9	1.3	10	4	3	2.7	3.4	0	2-14		5.6	5.8	15	1 -5		3.3	2.4
8	1	8	2.4	-1.7	10	4	4	2.2	-2.9	0	4-12		2.1	-3.0	15	1 -4		7.7	-6.8
8	1	9	3.0	3.5	10	4	5	3.2	3.0	0	5-14		2.1	-1.5	15	1 -2		2.7	1.4
8	1	11	1.9	0.7	10	5	2	2.8	2.6	1	0-18		2.3	-0.8	15	1 0		9.2	8.2
8	2	0	10.3	-10.6	11	0	4	2.7	-2.4	1	0-16		1.9	-1.4	15	2 -6		5.7	5.7
8	2	1	3.9	-3.6	11	1	0	7.9	7.1	1	0-12		4.0	3.6	15	2 -5		3.3	-2.5
8	2	3	4.6	4.1	11	1	4	4.2	-3.9	1	1-18		2.2	0.5	15	2 -2		9.1	-9.8
8	2	4	4.5	3.5	11	1	5	2.5	-2.6	1	1-17		2.1	1.2	15	3-11		2.7	1.9
8	2	6	3.7	-3.9	11	1	6	4.4	4.6	1	2-14		2.0	-1.1	15	3-10		2.2	-2.6
8	2	7	3.0	-3.1	11	1	8	3.7	3.5	1	4-13		2.9	2.0	15	3 0		2.0	-2.6
8	2	9	4.1	4.5	11	2	1	2.5	-2.9	2	0-12		3.9	-4.3	15	4-10		2.1	-0.9
8	3	3	2.7	-3.4	11	2	2	5.6	5.8	2	1-16		3.5	3.7	15	4 -6		2.3	-1.4
8	3	4	4.3	-4.5	11	2	5	4.8	5.6	2	1-12		6.7	-6.3	15	4 -2		3.2	2.9
8	3	5	2.7	-3.4	11	2	6	4.5	-5.1	2	2-18		2.5	-2.3	15	4 -1		2.5	1.5
8	3	8	2.1	2.5	11	2	8	2.0	2.1	2	2-14		4.9	4.7	16	0-12		2.5	-3.2
8	4	3	6.1	5.9	11	3	1	4.7	-5.0	3	0-18		2.6	0.8	16	0-10		2.4	2.7
8	4	5	2.3	-2.6	11	3	2	3.6	-3.1	3	0-16		2.3	-2.3	16	0 -8		3.9	4.1
8	4	6	6.5	-5.1	11	3	3	2.0	1.3	3	0-12		3.5	4.5	16	0 -4		3.2	-2.8
8	4	7	4.0	-4.7	11	3	4	2.2	-2.6	3	1-13		2.5	-2.7	16	0 0		2.4	2.6
8	5	1	3.1	2.4	11	3	6	4.7	4.7	3	1-12		2.9	2.4	16	1-10		3.1	-2.9
8	5	2	6.1	5.9	11	3	7	2.2	-1.1	3	2-15		2.0	-1.7	16	1 -9		2.7	2.6
8	5	4	3.0	4.3	11	4	1	3.5	-3.7	3	2-14		2.6	-3.6	16	1 -6		3.4	3.3
8	5	5	2.7	-3.0	11	4	2	9.2	-9.1	3	2-13		2.0	0.4	16	1 -2		3.5	-3.3
9	0	2	15.2	-15.5	11	5	0	7.9	8.0	3	4-13		2.3	2.1	16	2 -1		3.2	-1.6
9	0	6	2.7	2.6	12	0	2	2.3	-1.5	3	5-14		2.0	-1.4	16	2 0		4.8	-5.2
9	0	10	4.8	4.9	12	0	4	2.0	-2.3	4	1-15		3.5	3.7	16	3 -5		2.2	-1.6
9	1	0	4.9	4.2	12	1	1	6.9	-6.7	6	0-16		2.2	-2.2	16	3 -1		2.1	3.3
9	1	1	3.8	3.7	12	1	2	5.9	5.6	6	0-14		2.0	-2.4	16	4 -2		2.8	-1.5
9	1	2	1.9	2.0	12	1	3	7.4	-7.3	6	1-17		2.2	-1.1	16	4 -1		2.4	1.1
9	1	3	7.7	-7.4	12	1	4	2.4	1.7	6	1-13		2.0	1.9	16	5-10		2.6	-1.9
9	1	4	5.3	-4.6	12	1	5	3.8	3.9	6	1-12		3.3	-3.3	16	5 -9		2.7	1.7
9	1	5	4.9	-4.5	12	1	6	4.6	-4.8	6	2-12		2.4	-1.7	17	0-12		3.3	4.1
9	1	6	7.3	-6.4	12	1	7	2.4	2.6	6	3-15		2.3	-0.8	17	0 -8		3.8	-4.1
9	1	7	3.6	3.9	12	1	8	3.7	-2.6	6	3-14		2.4	2.0	17	0 -4		3.1	3.0
9	2	3	2.3	2.6	12	2	0	4.0	-4.2	6	4-15		2.2	1.4	17	1 -8		2.2	1.4
9	2	4	3.1	3.1	12	2	1	4.4	4.3	6	4-14		2.4	-4.8	17	1 -4		3.4	-2.8
9	2	7	3.6	-3.4	12	2	3	2.0	0.8	7	1-17		2.0	0.6	17	1 -2		2.0	0.9
9	2	8	6.1	-6.3	12	2	5	4.6	-4.7	7	1-12		2.8	3.1	17	1 -1		2.3	0.6
9	3	1	3.5	-3.0	12	2	7	3.2	-3.6	7	2-17		2.3	2.2	17	1 0		3.7	4.1
9	3	4	3.8	5.1	12	3	1	2.2	2.7	7	3-13		3.1	3.5	17	2-11		1.9	0.5
9	3	5	2.3	2.7	12	3	2	3.8	3.4	7	3-12		2.1	2.2	17	2 -6		3.2	2.2
9	3	6	5.5	6.2	12	3	3	4.6	4.9	7	5-14		2.2	-1.5	17	2 -2		4.1	-3.9
9	3	8	2.1	-2.6	12	4	0	3.9	3.9	8	0-16		2.1	-1.4	17	4 -4		2.0	0.9
9	3	9	4.0	-3.4	12	4	1	4.1	-4.0	8	0-12		3.4	2.7	17	4 -1		2.1	-1.5
9	4	1	6.4	-6.6	12	4	3	2.5	2.6	8	2-16		2.2	0.8	18	0-10		2.4	1.9
9	4	2	10.8	-11.0	13	0	2	2.7	2.3	8	3-14		2.0	2.7	18	0 -8		2.6	1.0
9	4	3	6.7	-6.7	13	0	4	3.1	-3.0	8	3-12		2.7	2.5	18	2 -3		2.2	2.1
9	4	5	4.1	4.3	13	0	8	3.7	4.4	8	4-14		3.5	-3.1	18	2 -2		2.1	0.9
9	4	6	4.6	4.1	13	1	0	6.3	5.3	9	2-14		2.6	1.2	18	3-10		2.1	1.1
9	4	7	3.1	3.0	13	1	1	6.3	-5.9	9	2-12		2.9	-3.3	18	3 -7		2.4	-1.6
9	5	0	5.5	5.3	13	1	3	3.0	2.7	9	3-12		2.5	1.2	18	4 -5		2.3	2.1
9	5	3	2.8	-2.7	13	1	4	5.3	-5.6	9	5-14		2.2	-1.1	18	4 -1		3.0	-2.5
9	5	4	5.7	-6.2	13	1	5	2.2	1.8	10	0-16		2.2	-3.4	18	4 0		2.1	2.3
10	0	0	4.1	-4.7	13	1	6	2.2	-1.0	10	0-12		2.8	3.4	19	1 -9		2.7	-1.2
10	0	2	3.6	-3.9	13	1	8	4.2	4.4	10	1-16		2.5	0.7	19	1 -7		2.1	2.6
10	0	4	3.9	4.6	13	2	1	5.6	-5.5	10	2-16		2.5	-1.1	19	2 -6		2.2	1.1
10	0	6	6.1	5.9	13	2	2	6.0	6.0	10	2-15		2.7	-1.7	20	0 -2		2.2	0.4
10	0	8	2.9	-3.0	13	2	3	5.7	-5.9	10	2-13		2.3	-3.0	20	0 0		2.4	-2.7
10	0	10	2.7	-3.4	13	2	6	4.5	-4.2	10	3-12		3.0	1.7	20	1 -9		2.1	-0.9
10	1	2	4.4	-4.2	13	2	7	3.6	3.1	11	0-14		2.4	-1.2	20	1 -1		2.5	-2.0
10	1	3	2.4	-2.2	13	3	4	3.4	3.1	11	1-15		2.3	1.5					

Table 5.5

Bond lengths (Å) and angles (degrees) in the α-picoline N-oxide residue (standard deviations in parentheses).

(a) X-ray analysis

N-O(1)	1.352(9)	C(1)-C(6)	1.506(12)
N-C(1)	1.354(10)	C(2)-C(3)	1.400(13)
N-C(5)	1.371(10)	C(3)-C(4)	1.367(13)
C(1)-C(2)	1.343(12)	C(4)-C(5)	1.339(13)
	O(1)·····O(1)^{I}	2.432(8)	

O(1) - N -C(1)	119.1(0.6)	C(3)-C(4)-C(5)	119.8(0.8)
O(1) - N -C(5)	118.9(0.7)	C(4)-C(5)-N	120.2(0.8)
N-C(1)-C(2)	117.8(0.8)	C(5) - N -C(1)	122.0(0.7)
C(1)-C(2)-C(3)	121.6(0.8)	C(2)-C(1)-C(6)	125.6(0.8)
C(2)-C(3)-C(4)	118.7(0.9)	C(6)-C(1)-N	116.6(0.7)
	N —O(1)····O(1)^{I}	107.7(0.7)	

(b) Neutron analysis

N-O(1)	1.345(18)	C(1)-C(6)	1.477(15)
N-C(1)	1.322(13)	C(2)-C(3)	1.381(17)
N-C(5)	1.350(13)	C(3)-C(4)	1.389(16)
C(1)-C(2)	1.396(17)	C(4)-C(5)	1.352(18)
	O(1)·····O(1)^{I}	2.428(27)	

Table 5.5 (cont'd)

C(2)-H(1)	1.13(4)	C(5)-H(4)	1.15(3)
C(3)-H(2)	1.08(4)	C(6)-H(5)	1.04(5)
C(4)-H(3)	1.04(3)	C(6)-H(6)	1.05(5)
	C(6)-H(7)	1.06(5)	

O(1)- N -C(1)	116.3(1.1)	C(3)-C(4)-C(5)	117.8(1.0)
O(1)- N -C(5)	120.0(1.1)	C(4)-C(5)- N	121.6(1.0)
N-C(1)-C(2)	116.0(0.9)	C(5)- N -C(1)	123.7(0.9)
C(1)-C(2)-C(5)	122.1(1.1)	C(2)-C(1)-C(6)	124.2(1.1)
C(2)-C(3)-C(4)	118.8(1.1)	C(6)-C(1)- N	119.8(1.1)
	N — O(1)·····O(1)^{I}	108.2(1.4)	

C(1)-C(2)-H(1)	117.5(2.0)	N-C(5)-H(4)	111.6(1.7)
C(3)-C(2)-H(1)	120.4(2.0)	C(1)-C(6)-H(5)	112.8(2.3)
C(2)-C(3)-H(2)	116.4(1.9)	C(1)-C(6)-H(6)	109.4(2.9)
C(4)-C(3)-H(2)	124.8(1.9)	C(1)-C(6)-H(7)	112.5(2.2)
C(3)-C(4)-H(3)	118.1(2.4)	H(5)-C(6)-H(6)	112.0(4.4)
C(5)-C(4)-H(3)	124.1(2.4)	H(5)-C(6)-H(7)	104.1(4.3)
C(4)-C(5)-H(4)	126.8(1.7)	H(6)-C(6)-H(7)	105.8(3.9)

Table 5.6

Comparison of the bond lengths of α-picoline-N-oxide determined from the present analysis with those published recently for some other pyridine N-oxides.

Molecule	Ref.	Av. ring C-C(Å)	Av. ring C-N(Å)	N-O(Å)
α-picoline-N-oxide	X-ray anal.	1.36	1.36	1.35
α-picoline-N-oxide	Neutron anal.	1.38	1.34	1.35
γ-picoline-N-oxide	16	1.379	1.343	1.349
γ-picoline-N-oxide	16	1.396	1.347	1.349
Pyridine-N-oxide	17	1.396	1.345	1.361
Pyridine-N-oxide	18	1.39	1.34	1.35

Table 5.7

Bond lengths (Å) and angles (degrees) in the hydrogen-bonded system involving the water molecules and bichloride ion. Standard deviations are in parentheses.

(a) X-ray analysis

Cl.....Cl^{I}	2.891(5)	Cl.....O(3)	3.062(8)
Cl.....O(2)	2.982(7)	O(2).....O(3)	2.723(8)

Cl^{I}.....Cl.....O(2)	119.2(0.2)	O(2).....Cl.....O(3)	81.6(0.2)
Cl^{I}.....Cl.....O(3)	118.4(0.2)	O(2).....O(3).....Cl	131.7(0.2)
O(3).....O(2).....Cl	129.9(0.2)		

(b) Neutron analysis

Cl.....Cl^{I}	2.950(19)	O(2) - H(8)	0.989(58)
Cl.....O(2)	2.984(18)	O(2) - H(9)	1.001(99)
Cl.....O(3)	2.969(19)	O(3) - H(10)	0.807(38)
O(2)....O(3)	2.777(19)	Cl - H(11)	0.714(42)

Cl^{I}.....Cl.....O(2)	119.1(0.5)	O(2).....O(3).....Cl	130.7(0.6)
Cl^{I}.....Cl.....O(3)	119.3(0.5)	H(8) - O(2) - H(9)	129.1(3.2)
O(3).....O(2).....Cl	131.0(0.6)	H(8) - O(2) - $H(8)^{I}$	101.8(3.2)
O(2).....Cl.....O(3)	81.7(0.6)	H(10) - O(3) - $H(10)^{I}$	123.0(3.5)

Position I is at $\frac{1}{2} - x, \frac{1}{2} - y, z$.

Table 5.8.

Intermolecular contacts which are less than the sum of the van der Waals radii of the atoms involved.

Symmetry-related positions other than x, y, z required to describe these contacts are :

I $-\frac{1}{2}-x, \frac{1}{2}-y, z$

II $-x, -\frac{1}{2}+y, \frac{1}{2}-z$

III $-x, 1-y, 1-z$

Atom A	Atom B	Distance (Å)		van der Waals distance (Å)
		x-ray anal.	neutron anal.	
C(6)	$C(6)^{I}$	3.60	3.63	4.0
C(6)	Cl^{II}	3.68	3.72	3.8
C(6)	Cl^{III}	3.74	3.74	3.8
C(5)	Cl	3.50	3.48	3.8
H(4)	Cl		2.40	3.0

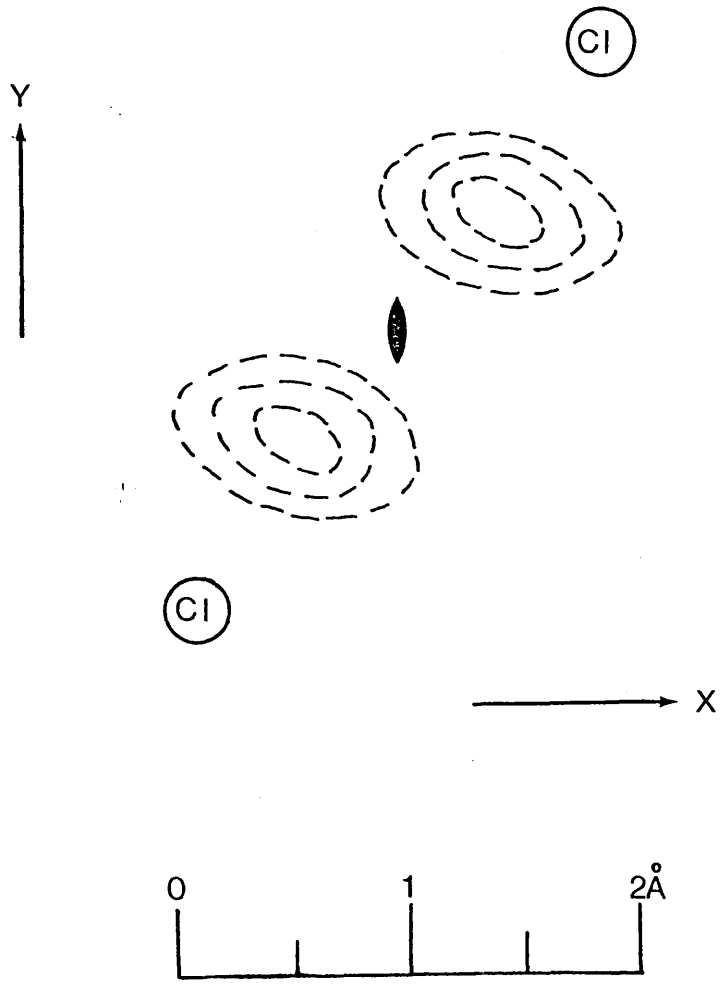


Figure 5.1 : The double minima of the bichloride ion proton, as shown in the difference map (section 5.4).

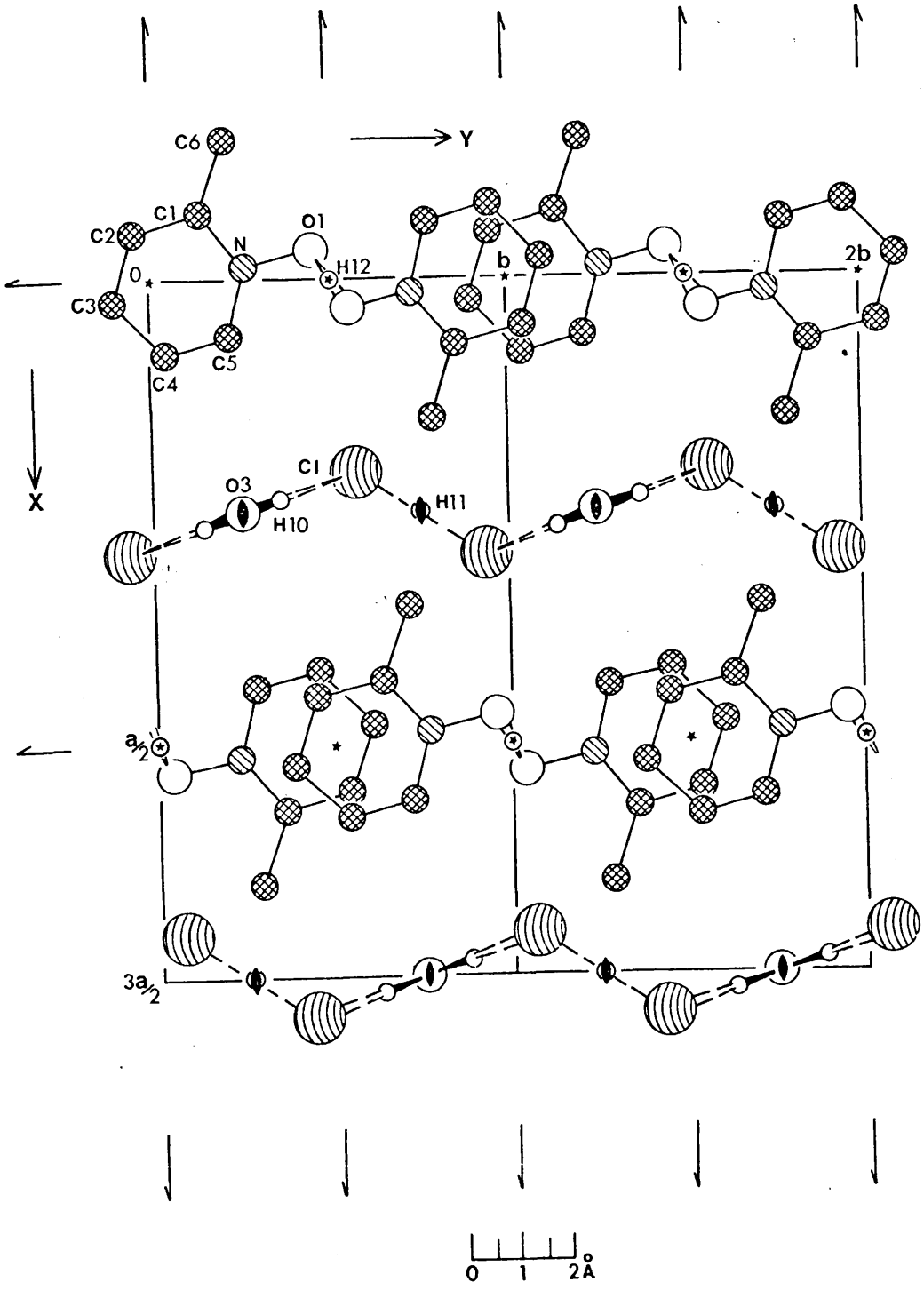


Figure 5.2 : The crystal structure of α-picoline N-oxide hydrochloride monohydrate projected along the c axis.

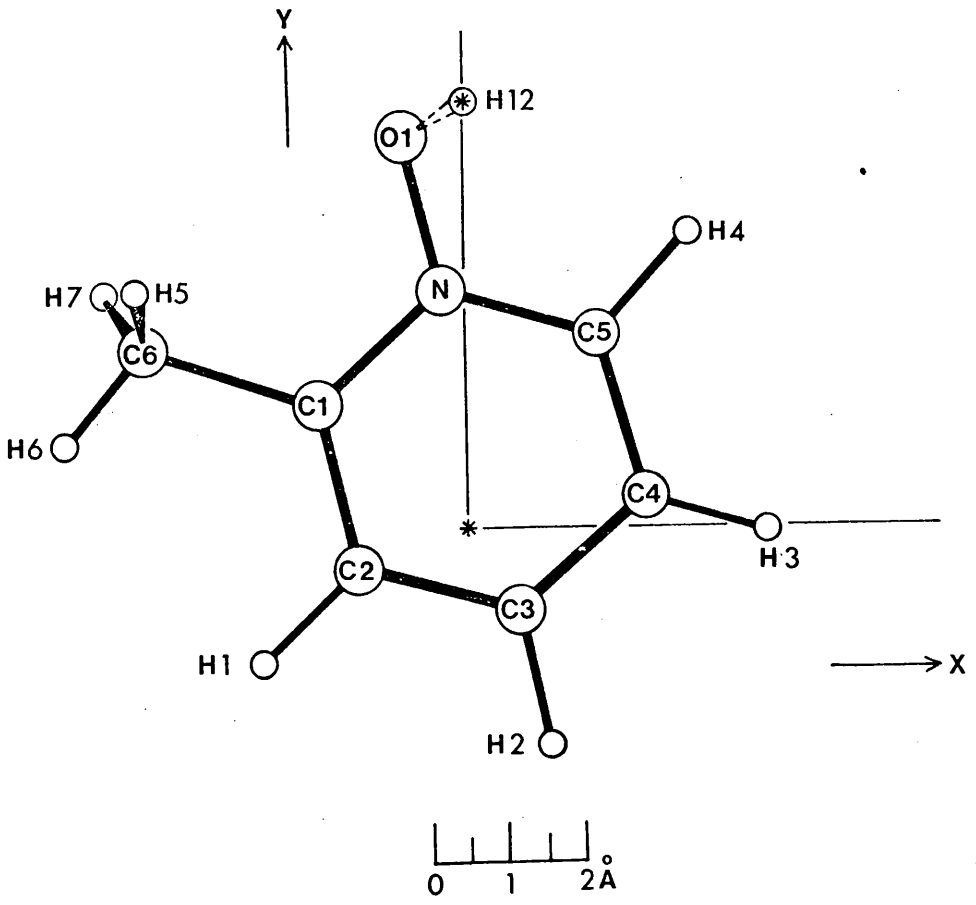


Figure 5.3 : The numbering system applied to the α-picoline molecule.

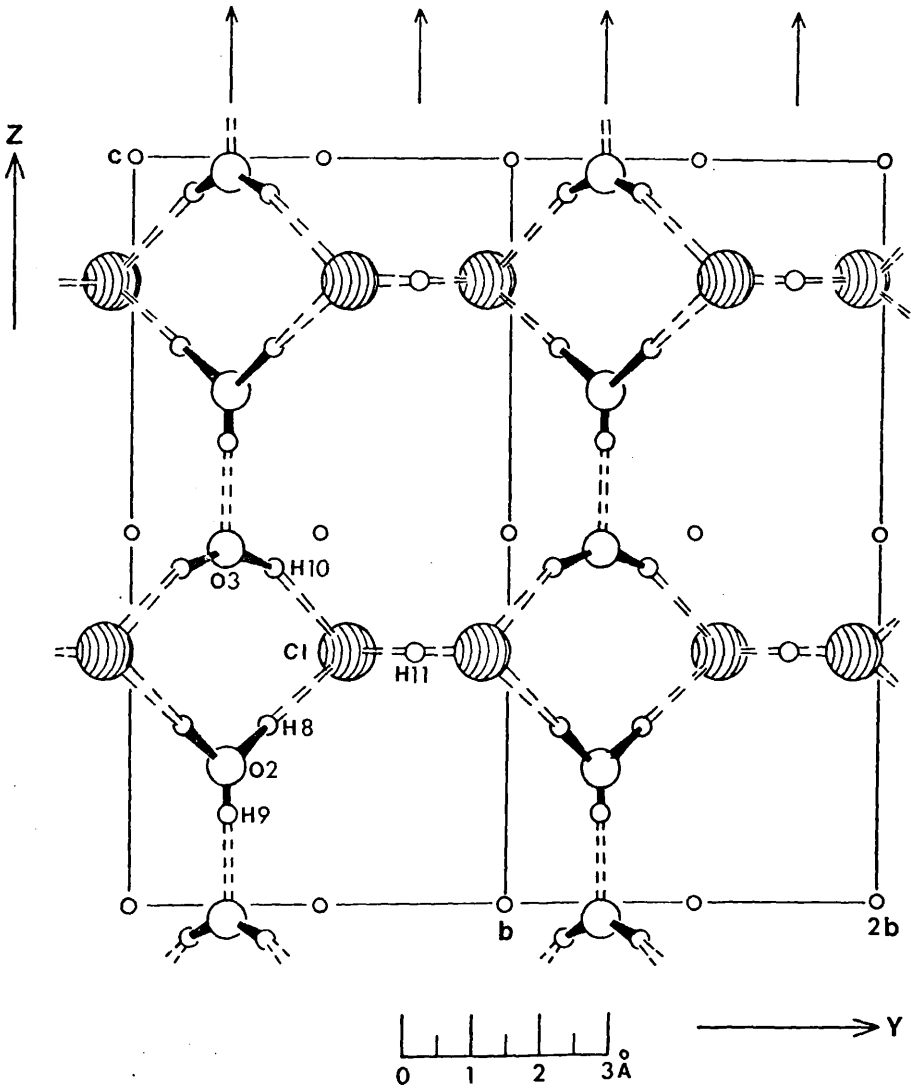


Figure 5.4 : The crystal structure of α-picoline N-oxide monohydrate projected along the a axis, showing the hydrogen bonding between the bichloride ions and the water molecules. The α-picoline N-oxide molecules have been omitted for clarity.

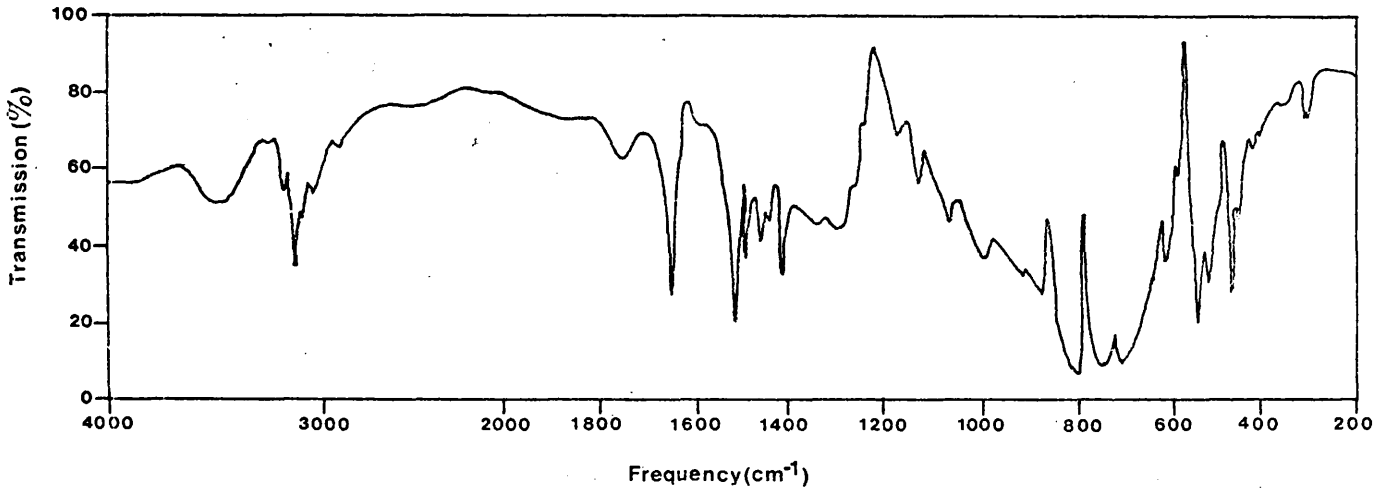


Figure 5.5 : The infra-red spectrum of α-picoline N-oxide hydrochloride monohydrate.(CsBr disc)

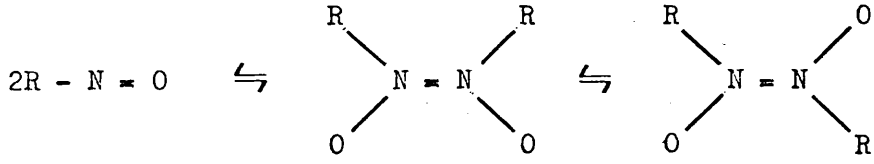
CHAPTER 6

THE CRYSTAL AND MOLECULAR STRUCTURES OF 9-NITROSOJULOLIDINE AND N,N-DIETHYL p-NITROSOANILINE.

6.1. Introduction

C-nitroso compounds

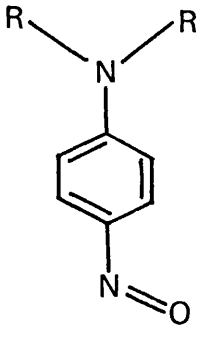
Although the chemistry of C-nitroso compounds has received considerable attention in recent years, there exists little detailed structural information about the C-nitroso group, especially the aromatic C-nitroso group. The main reason for this lack of structural knowledge of the nitroso group is that most C-nitroso compounds (which are blue if aliphatic and green if aromatic) exist in the solid state as colourless cis and/or trans dimers :



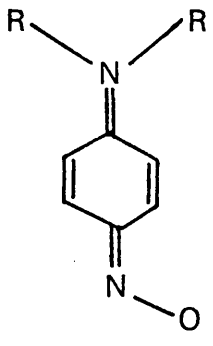
The only x-ray study of a monomeric nitroso compound which has been published is that of p-iodonitrosobenzene.[1] However, the analysis was carried out in projection, and this, combined with the presence of the strongly-scattering iodine atom, led to very high standard deviations in the bond lengths and angles.

Reasonably accurate structural parameters have been obtained for the simple aliphatic nitroso compounds CF_3NO[2] and CH_3NO[3] from gas-phase studies by electron diffraction and microwave spectroscopy respectively, but a microwave study of nitrosobenzene proved to be inconclusive because in order to obtain the C-N bond length and C-N-O angle, a value for the N-O bond length had to be assumed.

One group of aromatic nitroso compounds which are monomeric and form crystals eminently suitable for x-ray analysis are the p-nitrosoanilines (I). Since these were among the first nitroso compounds to be identified,[4] their physical and spectroscopic properties are well-known,[5] and have been interpreted in terms of a large contribution to the resonance hybrid of the quinonoid structure (II) :



(I)



(II)

An x-ray study of p-nitrosoanilines would thus provide information not only about the aromatic nitroso group, but also on the conformation of the amino group, and the extent to which structure (II) contributes to the resonance hybrid. A large contribution from (II) would be expected to result in the following structural features :

(1) C-N bond lengths considerably shorter than the C-N single bond length of 1.47 Å.

(2) A planar or almost planar amino group.

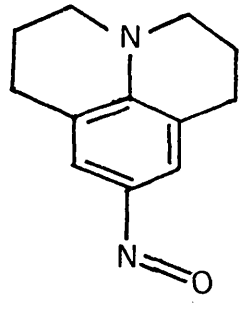
(3) The amino and nitroso groups essentially coplanar with the aromatic ring.

(4) The bonds between the ortho and meta positions of the aromatic ring shorter than the other ring bond lengths.

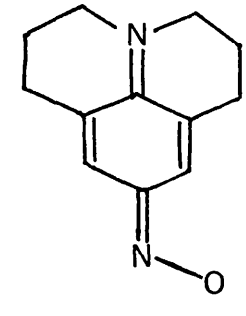
6.2. The Crystal and Molecular Structure of 9-nitrosojulolidine

6.2.1. Introduction

9-Nitrosojulolidine (III) was first synthesised in 1971 by MacNicol et al.[6] Crystals of the compound are well-formed prisms with a steel-blue lustre, although they are green to transmitted light, as expected of an aromatic nitroso monomer. An n.m.r. study[6] of the internal rotation in 9-nitrosojulolidine showed an appreciable barrier to rotation of the nitroso group about the C-N bond ($\Delta H^{\ddagger}$ = 17.1 kcal.mole^{-1}), indicating a substantial contribution by the quinonoid structure (IV) to the resonance hybrid :



(III)



(IV)

An x-ray analysis of 9-nitrosojulolidine was undertaken for the reasons discussed at the end of section 6.1., and in addition, to ascertain the conformation of the quinolizidine skeleton and the extent to which,

if at all, it prevents the amino group from achieving coplanarity with the aromatic ring.

6.2.2. Experimental

Crystal Data

$C_{12}H_{14}N_2O$, M = 202.17. Monoclinic, $\underline{a}$ = 7.448 (4), $\underline{b}$ = 8.717 (5), $\underline{c}$ = 15.890 (9), $\underline{\beta}$ = 100.3 (0.1)°. $\underline{U}$ = 1015.0 Å^3, $\underline{D}_m$ = 1.31, $\underline{z}$ = 4, $\underline{D}_c$ = 1.323. $\underline{\mu}(M_oK_\alpha)$ = 1.0 cm^{-1}. Space group $P2_1/C$ (No. 14).

Data Collection

A cubic crystal of dimensions 0.6 x 0.6 x 0.6 mm^3 was mounted along its $\underline{b}$-axis and the space-group and initial cell dimensions were obtained from rotation, Weissenberg and precession photographs taken using CuK_α radiation. More accurate cell dimensions were obtained by a least-squares treatment of a number of high-order reflections for which θ values had been measured on a four-circle diffractometer using MoK_α radiation.

Integrated intensities were measured automatically on a P.D.P. 8 controlled Hilger and Watts four-circle diffractometer for reflections out to $\theta = 25°$. Lorentz and polarisation corrections were applied to the data, but absorption corrections were not considered necessary. The 847 reflections for which $|F| > 3\sigma(|F|)$ were used in the subsequent analysis.

6.2.3. Structure Analysis and Refinement

The structure was solved by the symbolic addition method, but only after some difficulty. Normalised structure factors were calculated for the 847 observed reflections, and an origin was defined by assigning positive signs to the reflections 612, 357, and 457. Using the XRAY 70 programm PHASE, a unique solution was obtained without having to assign any symbolic phases. Of the 110 reflections with $|E| \geq 1.5$ used in the solution, phases were obtained for 104, and the E-map which was calculated using these 104 phased E's as coefficients is shown in Figure 6.2.1. It can be seen that there are too many peaks, and this is a common feature of E-maps. Fortunately, it was possible to select only two, equally plausible, sets of peaks corresponding to 9-nitroso-julolidine from the E-map. Each set of co-ordinates gave an R-value of about 60 per cent, which least squares refinement could not lower below 45 per cent; clearly, neither set of co-ordinates was the correct solution. Symbolic addition calculations were then carried out using different origin-defining reflections, but the result was merely to reproduce the same set of E-map peaks at different locations in the unit cell, and R-values for sets of plausible peaks ranged from 65 to 80 per cent. Suspect reflections - one and two dimensional reflections which entered into a large number of Σ_2 relationships - were removed from the solution, but again with no success. However, on closer inspection of the initial solution, it was noticed 6 peaks were common to both the sets of

peaks selected from the E-map, and that these six peaks were, on average, about twice the height of the others. This could be explained by two overlapping half-weight images of 9-nitrosojulolidine separated by an aromatic C-C bond length, as shown in Figure 6.2.2. A similar effect has been reported by Bürgi and Dunitz[7] in the structure analysis of p-methyl benzylidene-p-nitroaniline; the correct solution was an average of two molecular images which were separated by a multiply-occurring interatomic vector. The two sets of 9-nitroso-julolidine co-ordinates were thus averaged, and the co-ordinates thus obtained gave an R-value of 45 per cent, which reduced to 19 per cent after three cycles of full-matrix, isotropic, least-squares.

This 'double-image' effect is an unavoidable result of the limitations of the symbolic addition method when applied to structures containing translational regularities such as six-membered rings. In these circumstances symbolic addition is unable to distinguish between various pseudo-homometric structures because only the strongest $|E|$ values can be used. (The Patterson functions of these pseudo-homometric structures, although different, would be almost identical if computed exclusively with the largest values of E^2). However, this limitation should not be a threat to the application of symbolic addition methods to symmetrical structures, especially those with centrosymmetric space groups, since the detection of a 'double image' effect should lead in a straightforward manner to the correct solution (providing of course, that the images are at the correct location in the unit cell).

At the end of the isotropic least-squares refinement, a difference map was calculated, which revealed all the hydrogen atoms in their expected positions, as well as disorder in the nitroso group and in one of the trimethylene chains. These features are shown in Figure 6.2.3. along with the atomic numbering system. Refinement was completed with four cycles of anisotropic least squares, in which the block-diagonal approximation was used for all but six of the atoms; because of the high correlations involved, atoms O(1), O(1'), N(1), C(11), C(11') and C(2) were refined by full-matrix least-squares. (N(1') was considered too close to N(1) to be refined - its co-ordinates were fixed at the values obtained from the difference map, but it was accorded the same population and isotropic thermal parameters as N(1)). The disordered atoms O(1), O(1'), N(1), C(11) and C(11') had isotropic temperature factors (U) and population parameters (P) refined, as well as their positional parameters. The following constraints were applied during refinement to these thermal and population parameters :

$$P[O(1)] + P[O(1')] = 1 \qquad U[O(1)] = U[O(1')]$$

$$P[N(1)] = P[O(1)] \qquad U[N(1)] = U[N(1')]$$

$$P[N(1')] = P[O(1')]$$

$$P[C(11)] + P[C(11')] = 1$$

The R-value at the end of the refinement was 8.3 per cent. The following weighting scheme was applied during the final cycles of least-

squares refinement :

$$W = X \times Y$$

If $A \times F_{obs} > |F_{calc}|$ $\quad w = 0.000000001$

If $\sin\theta > B$, $\quad x = 1$, $\quad$ else $x = \sin\theta / B$

If $C > F_{obs}$ $\quad y = 1$, $\quad$ else $y = C/F(obs)$

and the final values of A, B and C were 0.3, 0.5 and 12.0 respectively.

The final atomic co-ordinates and vibrational parameters are listed in Tables 6.2.1. and 6.2.2. respectively. The observed structure amplitudes and corresponding calculated structure factors are listed in Table 6.2.3.

6.2.4. Description and Discussion of the Structure

The bond lengths and angles in 9-nitrosojulolidine are listed in Tables 6.2.4. and 6.2.5. respectively, and confirm the expected large contribution of the quinonoid structure (IV). In particular, the two C-N bond lengths of 1.350(6) Å and 1.434(9) Å (C(5)-N(2) and C(2)-N(1) respectively) are significantly shorter than the accepted C-N single bond length of 1.47 Å. The C(5)-N(2) distance of 1.350 Å can be compared with similar very short C-N bonds of 1.35(2) Å in N,N-dimethyl-p-nitroaniline,[8] and 1.37(1) Å in p-nitroaniline.[9]

The dimensions of the aromatic ring suggest a quinonoid-type structure, but the differences between bonds C(6)-C(1), C(1)-C(2), C(2)-C(3) and C(3)-C(4) are not statistically significant. However,

the bonds at the amino end of the ring - C(4)-C(5) and C(5)-C(6) - are significantly longer than the other ring bonds, and this is a feature found also in both p-nitroaniline and N,N-dimethyl-p-nitroaniline. The aromatic ring is planar within the limits of experimental error, and the equation of the mean plane through the ring is given in Table 6.2.7. along with the displacements of the atoms from the plane. The displacements of C(9), N(2) and C(10) from the plane by +0.14 Å, +0.03 Å and +0.09 Å respectively, indicate that the amino group.is non-planar. However, the deviation from planarity is small, and is probably the result of crystal packing forces, rather than any residual sp^3 character in the nitrogen bonding orbitals.

The nitroso group dimensions, which have been less accurately determined than had been hoped because of the disorder described in section 6.2.3, also reflect a large contribution from structure (IV). The C-N and N-O bond lengths of 1.434(9) Å and 1.245(11) Å respectively can be compared with those in nitrosomethane of 1.48 Å and 1.21 Å. Since the C-N-O angle in structures III and IV is of the type $X{=}\ddot{N}{-}Y$ in both cases, a large contribution of IV to the electronic structure of III would not be expected to have much effect on the C-N-O angle; the value determined for the angle C(2)-N(1)-O(1) of 112.8° agrees well with the normal value for an $X{=}\ddot{N}{-}Y$ angle[10] of 113°.

To enable efficient overlap of the C(2) and N(1) $p\pi$ orbitals, the nitroso group has to be more or less coplanar with the aromatic ring. It makes an angle of only 2.8° with the plane of the ring, and in order

to relieve what would otherwise be a very short intramolecular contact between O(1) and H(2) of about 2.4 Å, angle C(3)-C(2)-N(1) has opened to 128°. The resulting O ···· H distance of 2.63(6) Å corresponds to a normal van der Waals contact (2.6 Å).

The trimethylene chains of the quinolizidine adopt the expected conformations, with C(11) above, and C(9) below, the plane of the molecule. The resulting torsion angles are given in Table 6.2.8. The conformations of the two fused six-membered rings of the quinolizidine skeleton can be likened to the 'envelope' conformation of cyclopentane with only one atom markedly out of plane with the others; in one ring the envelope flap is pointing upwards, in the other ring, downwards. This 'up-down' conformation is, however, adopted by only 63 per cent of the julolidine molecules; in the other 37 per cent, both rings have their envelope flaps pointing downwards, and it is this disorder (of C(11)) which determines the amount of disorder in the nitroso group. Figure 6.2.4. shows the packing of the nitrosojulolidine molecules in the unit cell as viewed down $\underline{a}^*$. It can be seen that the molecules pack in centrosymmetric head-to-tail pairs, in which the nitroso group of one molecule fits neatly into the amino end of the centrosymmetrically-related molecule. The orientation which the nitroso group adopts is therefore greatly influenced by the conformation of the quinolizidine skeleton. In the case of the predominant conformation, in which one flap is up and the other down, the nitroso group points in the direction of the downward flap, (the alternative orientation, 180° away,

would involve a very short O .... CH_2 contact of 3.41 Å). In the case of the minor conformation, in which both flaps point downwards, there is little difference energetically between the two orientations, and the nitroso group adopts each orientation to an equal extent. The resulting populations of the two orientations should thus be in the ratio $63 + \frac{1}{2} \times 37 : \frac{1}{2} \times 37 = 81.5 : 18.5$. The ratio of the population parameters obtained from the least-squares refinement is 83:17.

The disorder of the trimethylene chain involving atoms C(10), C(11) and C(12) has resulted in unsatisfactory bond lengths and angles between these atoms, and the large vibrational amplitudes (about 0.1 Å) of the other trimethylene chain involving atoms C(7), C(8) and C(9) has caused an apparent shortening in the bond lengths of C(7)-C(8) and C(8)-C(9) from the normal C-C bond length of 1.54 Å to 1.48 Å and 1.50 Å respectively.

All the intermolecular distances in the structure correspond to normal van der Waals contacts, but the shortest contacts involving the nitroso group are listed in Table 6.2.8. The aromatic rings of the centrosymmetrically-related head-to-tail pairs of nitrosojulolidine molecules are 3.70 Å apart. This is 0.3 Å more than the normal van der Waals contact distance between aromatic rings, the increase being due to the bulky trimethylene chains in the quinolizidine end of the molecules.

TABLES AND DIAGRAMS

Table 6.2.1

Final fractional co-ordinates (x, y, z) with population parameters (p) other than unity. Standard deviations are in parentheses.

	x	y	z	p
N(1)	-0.3292(12)	0.7968(9)	0.3888(6)	0.83(2)
N(1')	-0.365	0.817	0.405	0.17(2)
N(2)	0.2256(6)	0.8124(5)	0.6744(3)	
O(1)	-0.4721(8)	0.8682(7)	0.3922(4)	0.83(2)
O(18)	-0.3715(40)	0.7830(34)	0.3482(21)	0.17(2)
C(1)	-0.0404(8)	0.7313(7)	0.4662(3)	
C(2)	-0.2019(8)	0.8058(7)	0.4686(3)	
C(3)	-0.2202(7)	0.8831(7)	0.5433(4)	
C(4)	-0.0823(8)	0.8847(7)	0.6135(4)	
C(5)	0.0846(7)	0.8099(6)	0.6082(3)	
C(6)	0.1006(7)	0.7317(6)	0.5316(3)	
C(7)	0.2992(9)	0.6560(8)	0.5238(4)	
C(8)	0.3844(10)	0.6111(9)	0.6078(5)	
C(9)	0.4019(8)	0.7449(9)	0.6680(4)	
C(10)	0.2176(9)	0.8971(9)	0.7535(4)	
C(11)	0.0793(16)	1.0072(14)	0.7471(6)	0.63(3)
C(11')	0.0196(40)	0.9536(34)	0.7575(16)	0.37(3)
C(12)	-0.0977(11)	0.9607(11)	0.6971(6)	

Table 6.2.1. (cont'd)

	x	y	z
H(1)	-0.029(8)	0.683(7)	0.413(4)
H(2)	-0.319(8)	0.931(7)	0.551(4)
H(3)	0.245(8)	0.562(7)	0.483(4)
H(4)	0.339(8)	0.716(7)	0.490(4)
H(5)	0.505(8)	0.580(7)	0.595(4)
H(6)	0.324(8)	0.521(7)	0.639(4)
H(7)	0.502(8)	0.830(7)	0.644(4)
H(8)	0.459(8)	0.728(7)	0.715(4)
H(9)	0.340(8)	0.934(7)	0.767(4)
H(10)	0.226(8)	0.826(7)	0.806(4)
H(11)	0.062(8)	0.045(7)	0.815(4)
H(12)	0.107(8)	0.082(7)	0.715(4)
H(13)	-0.154(8)	0.900(7)	0.720(4)
H(14)	-0.195(8)	1.026(7)	0.687(4)

Table 6.2.2.

Vibrational parameters ($Å^2$) with standard deviations in parentheses.

	U_{11} or U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	0.082(2)					
N(2)	0.058(3)	0.057(3)	0.053(2)	-0.005(2)	0.005(2)	0.001(2)
O(1)	0.088(3)					
C(1)	0.065(4)	0.073(4)	0.050(3)	0.002(3)	0.009(3)	0.005(3)
C(2)	0.066(4)	0.058(3)	0.057(3)	-0.009(3)	0.004(3)	0.012(3)
C(3)	0.045(3)	0.054(3)	0.098(4)	0.007(3)	0.013(3)	0.016(3)
C(4)	0.060(4)	0.061(4)	0.071(4)	0.003(3)	0.015(3)	-0.009(3)
C(5)	0.050(3)	0.038(3)	0.055(3)	-0.005(2)	0.009(2)	0.004(2)
C(6)	0.056(3)	0.046(3)	0.055(3)	-0.051(2)	0.007(2)	0.001(2)
C(7)	0.073(4)	0.083(5)	0.070(4)	0.014(4)	0.017(3)	-0.005(3)
C(8)	0.075(4)	0.094(5)	0.092(5)	0.030(4)	0.015(4)	0.003(4)
C(9)	0.050(4)	0.104(5)	0.080(4)	0.006(3)	-0.007(3)	0.007(4)
C(10)	0.082(4)	0.095(5)	0.061(4)	-0.014(4)	0.004(3)	-0.015(4)
C(11)	0.064(4)					
C(12)	0.083(5)	0.130(7)	0.123(6)	0.020(5)	0.026(4)	-0.044(6)
H(1)	0.06					
H(2)	0.07					
H(3)	0.08					
H(4)	0.08					
H(5)	0.09					

Table 6.2.2. (cont'd)

	U_{iso}
H(6)	0.09
H(7)	0.08
H(8)	0.08
H(9)	0.08
H(10)	0.08
H(11)	0.06
H(12)	0.06
H(13)	0.11
H(14)	0.11

Table 6.2.3

Observed structure amplitudes and final calculated structure factors. (×10)

7,5,L

4	32	-58
3	47	-62
-1	46	62
-2	33	-49
-10	40	65

7,4,L

5	39	61
4	35	-73
3	30	38
2	29	-7
1	36	-44
-3	36	78
-9	51	-50

7,3,L

1	84	-104
0	73	79
-1	80	-61
-2	46	46
-3	38	91
-4	44	35
-7	38	-88

7,2,L

1	33	54
-1	58	-68
-2	63	48
-4	63	-96
-5	30	-45

7,1,L

7	32	-31
5	29	-21
3	31	37
2	58	-91
1	91	78
-6	34	-63
-8	38	-52
-11	35	-43

7,0,L

6	42	103
-6	42	41
-8	42	-137
-10	33	29
-14	42	51

6,6,L

-1	36	-19
-9	39	49

6,5,L

4	43	47
-1	40	-42
-3	79	-81
-6	48	63
-7	31	-28

6,4,L

7	30	64
6	57	-52
3	29	-23
-8	65	86
-10	37	61
-12	31	-25

6,3,L

8	51	106
6	30	-32
-9	29	43
-12	36	-46
-13	38	32
-14	45	-94

6,2,L

8	31	-11
7	54	-101
6	61	92
-1	78	-154

6,1,L

-4	79	-95
-6	45	-114
-7	48	-55
-8	28	19
-10	88	99
-12	148	210
-13	43	-23

6,0,L

10	45	79
8	34	-45
6	45	-51
-2	59	63
-4	78	-88
-10	50	-69
-14	56	92

5,8,L

0	32	-1
-1	32	60

5,7,L

4	47	-47
0	59	98
-2	60	74
-7	39	32

5,6,L

5	44	35
1	71	-119
-1	73	-77
-2	46	67
-4	31	-23
-5	30	31
-7	36	-13

5,5,L

6	31	-56
5	53	-43
-1	28	-48
-6	28	-39
-7	53	-51

5,4,L

7	42	82
1	66	65
0	32	21
-1	41	63
-3	29	-128
-4	40	-98
-6	78	129
-7	47	-86
-8	30	-25
-9	32	5
-10	47	50
-15	38	-39

5,3,L

10	31	-17
9	56	-38
6	51	34
5	188	222
4	215	259
3	103	76
0	64	-62
-1	41	-29
-3	69	90
-5	121	120
-8	66	-17
-9	148	-204
-10	107	-173
-11	38	-33

5,2,L

8	91	123
7	45	-56
6	35	-12
5	49	-92
3	98	132
2	124	155
0	46	22
-1	38	63
-2	55	82
-3	24	-49
-5	83	92
-6	139	-180
-7	83	84
-8	30	23
-9	68	121
-10	28	46
-11	79	-71
-12	54	-129

5,1,L

10	71	-106
9	58	99
8	33	-39
7	48	-71
6	52	-47
5	93	-107
4	142	-143
3	135	-104
2	58	-34
1	69	165
0	31	62
-1	44	-27
-2	112	-144
-3	80	-39
-4	98	141
-5	75	-172
-6	95	134
-7	46	57
-8	35	40
-9	97	127
-10	149	147
-11	41	34
-12	86	77
-13	41	-89

5,0,L

10	86	-82
8	112	-102
4	78	27
2	76	-241
0	23	-91
-2	34	-195
-4	52	68
-6	152	231
-8	48	-36
-10	111	-112
-12	97	209
-14	31	68

4,8,L

6	91	-127
2	34	96
-6	49	43
-7	37	-21
-8	53	91
-9	31	-67

4,7,L

7	42	63
5	67	113
4	38	4
2	54	114
0	35	74
-3	32	109
-7	41	-56
-9	53	-73

4,6,L

7	38	-57
6	97	132
5	50	-2
3	34	-78
0	61	85
-2	30	78
-8	63	-71
-13	45	48

4,5,L

10	29	-6
8	63	-118
7	162	-187
6	186	-136
5	124	-104
4	28	16
2	41	-43
1	86	178
0	72	-88
-1	27	-66
-2	25	-41
-4	30	-9
-5	38	-132
-6	92	113
-7	194	225
-8	92	146
-9	67	78
-13	33	-71

4,4,L

12	45	-93
11	36	-53
7	47	72
6	32	20
5	63	-112
4	104	-153
2	85	-191
1	83	-2
0	144	-136
-2	43	150
-3	36	-18
-5	36	35
-6	117	-112
-7	106	-141
-8	38	-69
-9	78	65
-10	97	156
-12	31	23
-14	34	-3

4,3,L

8	54	67
7	72	48
6	148	207
5	103	83
4	24	-30
3	87	-148
1	90	92
-2	64	110
-4	125	-54
-6	86	-78
-7	83	-87
-8	186	-221
-9	147	-120
-10	29	17
-11	32	60
-13	54	-65

4,2,L

12	43	75
11	83	70
10	46	106
4	61	146
3	34	116
2	104	92
1	117	-52
-1	32	161
-2	24	-72
-3	118	-115
-4	169	-266
-5	74	78
-7	76	69
-8	89	52
-10	94	-170
-11	58	-103
-12	45	-73

4,1,L

12	74	-71
10	54	-34
8	43	53
7	37	-28
5	78	65
3	34	-2
2	97	9
1	89	-38
0	56	-141
-1	30	11
-2	329	274
-3	58	177
-4	200	195
-6	34	-83
-9	31	36
-10	80	138
-11	42	-5
-15	54	-93
-18	33	-56

4,2,L

10	114	-164
8	39	-57
2	104	-21
-4	453	431
-6	110	164
-12	41	89

3,9,L

3	31	-58
-3	42	67
-4	36	23
-6	58	95

3,8,L

8	57	-97
6	34	-3
-5	97	115
-7	60	-117

3,7,L

9	59	108
8	124	139
7	78	74
5	35	5
1	37	111
-2	33	74
-4	78	-38
-5	105	-146
-6	121	-194
-7	54	-51
-9	34	-6

3,6,L

9	104	-162
8	97	152
7	68	-43
6	51	74
4	28	27
3	31	118
2	36	71
-1	46	-101
-2	39	-64
-5	238	292
-6	118	-152
-7	34	55
-8	108	-113
-9	28	-71

3,5,L

10	62	-83
9	56	-46
7	142	-224
6	30	57
5	61	167
4	58	-92
3	26	67
2	33	-56
0	60	167
-1	62	-164
-2	45	96
-3	68	31
-4	38	96
-5	121	186
-6	63	93
-7	253	264
-9	63	-157
-10	48	97
-12	59	88

3,4,L

14	47	-66
13	41	-64
12	35	-19
10	38	-55
9	122	122
8	48	-135
6	51	-154
5	37	-56
3	52	38
2	47	-124
1	45	-43
0	138	103
-1	139	149
-2	24	48
-3	51	116
-6	148	-180
-7	78	-18
-8	139	258
-9	81	119
-10	36	31
-11	48	-17
-12	33	53

3,3,L

14	32	51
13	53	51
12	31	56
11	41	-98
9	53	25
8	75	-78
6	49	-1
5	49	-18
4	49	96
3	166	-155
2	282	256
1	47	75
0	262	-259
-1	258	-271
-2	65	-187
-3	34	134
-4	68	-132
-5	75	-34
-6	125	63
-7	47	-68
-8	56	-84
-10	89	-94
-11	66	66
-12	39	-118
-15	54	95
-17	38	-12

3,2,L

9	32	61
6	38	18
5	98	-149
4	73	128
3	313	-248
2	150	49
1	72	182
0	60	-115
-1	129	17
-2	242	-298
-3	312	-234
-4	46	-45
-5	118	-139
-6	33	-32
-7	25	-11
-8	25	-124
-9	58	7
-10	76	-92
-11	83	73
-12	27	-16

3,1,L

13	48	-26
9	44	57
8	26	-68
6	48	-74
5	111	49
4	28	-189
3	21	-110
2	63	-48
1	64	79
-1	387	178
-2	275	136

Table 6.2.3 (cont'd)

3,1,L

-3	87	-18
-4	47	-113
-5	85	-97
-9	44	37
-11	38	31
-12	45	-13
-13	31	-38
-16	44	-47

3,0,L

14	28	-46
10	35	-72
8	47	79
4	337	-130
2	123	-57
0	40	157
-2	312	466
-4	210	167
-6	60	14
-8	66	26
-10	104	91
-14	27	21
-16	54	-103

2,10,L

0	54	-38
-1	32	11

2,9,L

1	32	38
-2	36	47
-3	75	114
-4	86	110

2,8,L

9	33	-26
4	30	-80
2	66	108
0	56	117
-2	57	-80
-3	59	-102
-6	70	110
-9	31	47

2,7,L

10	65	89
4	36	-93
1	63	-112
0	64	137
-1	82	-152
-3	26	-14
-4	191	-233
-5	52	-57
-6	42	29

2,6,L

11	35	-35
9	59	-46
8	72	109
6	47	-39
2	118	-164
1	88	-113
0	65	-97
-1	24	8
-3	133	146
-4	71	-99
-6	164	97
-8	165	-241
-7	68	-176

2,5,L

8	65	61
5	26	-38
3	45	-144
2	165	188
1	152	137
0	25	-27
-1	51	115
-2	38	5
-3	67	-39
-4	42	56
-5	24	58
-6	46	-21
-7	45	36
-12	49	-124

2,4,L

11	87	98
10	198	-287
9	131	142
7	52	-53
5	82	29
4	60	116
3	22	-7
2	69	-142
1	107	141
0	173	132
-1	139	176
-2	154	93
-3	321	-232
-4	579	600
-5	253	-238
-6	65	54
-8	31	-73
-9	34	-14
-11	34	-45
-12	48	158
-13	34	-42
-14	29	-44
-15	30	-54
-16	33	-45

2,3,L

14	32	43
12	56	73
10	100	-113
9	158	185
8	57	-51
7	68	-54
6	78	100
5	80	-60
3	28	112
2	149	-188
1	73	174
0	258	-223
-1	54	64
-3	40	59
-4	269	219
-5	228	-174
-6	104	14
-7	132	90
-8	60	-202
-9	81	93
-10	71	-107
-11	37	-17
-12	83	122

2,2,L

12	89	112
11	127	-145
10	91	111
9	68	-131
8	38	52
7	47	-87
6	226	93
5	187	168
4	148	127
3	23	-38
2	65	-208
1	57	-49
0	55	1
-1	373	-515
-2	232	-163
-3	231	265
-4	127	-251
-5	197	189
-6	149	-138
-7	50	53
-8	77	-41
-10	68	-64
-11	38	28
-12	41	7
-15	63	117

2,1,L

13	41	74
11	47	-36
10	66	37
9	43	-75
8	46	-84
7	113	-77
6	257	-289
5	183	203
4	163	-97
3	33	38
2	69	115
1	51	90
0	179	99
-1	124	-48
-2	38	59
-3	37	-6
-4	213	258
-5	237	-199
-7	37	77
-8	44	-21

2,0,L

12	43	-42
10	40	44
8	57	-42
6	448	-543
4	572	-542
2	393	605
0	105	117
-2	621	-384
-4	146	-147
-6	37	173
-8	336	298
-10	175	82
-12	59	-178
-14	37	-45

1,10,L

-4	33	-29

1,9,L

4	30	21
-2	63	73
-3	78	104

1,8,L

10	30	-57
7	32	-19
4	60	67
2	71	71
-1	48	-56
-2	40	-11
-4	39	117
-5	36	66
-10	44	-35

1,7,L

10	30	0
8	49	-37
4	70	-52
3	85	-111
2	46	89
1	58	-97
-5	43	-90
-6	42	82
-9	34	28
-11	53	84

1,6,L

14	37	-12
6	34	-9
4	74	-68
3	91	121
2	158	-167
1	38	-15
-1	47	-75
-2	36	-86
-5	27	8
-7	28	79
-11	33	-91
-12	68	100

1,5,L

10	27	-11
7	32	-41
6	51	44
5	57	-195
4	34	-37
3	235	215
2	56	-273
1	211	235
-1	71	-38
-2	156	133
-3	165	-145
-4	26	-49
-5	25	163
-6	81	-73
-11	87	-103
-13	34	-76
-16	42	-58

1,4,L

14	44	-84
11	61	83
10	42	16
9	55	-78
8	43	35
7	106	-48
6	128	-119
5	54	-15
4	51	148
3	98	-33
2	27	100
0	227	238
-1	137	-146
-2	247	273
-3	358	-268
-4	176	51
-5	59	87
-8	87	122
-9	26	-31
-10	36	12
-11	35	-20
-12	42	-87
-14	53	-85
-16	48	-71
-17	51	78

1,3,L

13	37	-17
12	32	19
10	29	-43
9	104	124
8	174	192
7	22	53
6	61	-183
5	131	212
2	62	12
1	272	-269
0	98	39
-1	235	187
-2	185	-132
-3	42	-42
-4	118	154
-5	244	-222
-6	211	-284
-8	128	183
-9	78	-189
-13	29	16
-15	32	-58

1,2,L

14	64	78
13	83	-145
12	191	234
11	175	-298
10	38	-14
9	122	189
8	169	163
7	273	377
6	159	17
5	53	-34
4	53	-88
3	164	-353
2	21	-13
1	126	-92
0	124	52
-3	734	647
-4	78	-43
-5	73	-235
-6	244	-93
-7	357	-351
-8	169	-73
-9	96	288
-10	33	-53
-11	32	139
-15	79	-159
-16	83	128
-17	44	-72

1,1,L

14	62	-123
13	71	64
12	159	189
11	97	-124
10	59	32
8	288	-255
7	137	-118
6	59	-44
4	241	462
3	158	-253
2	76	187
1	37	186
0	248	628
-1	279	-361
-2	557	-377
-3	527	449
-4	39	81
-5	65	-18
-6	521	568
-7	185	184
-8	152	138
-9	98	-72
-10	85	-168
-11	87	112
-12	53	-2
-15	31	48

1,0,L

14	138	-132
12	286	-242
10	132	-185
8	189	-119
6	35	-25
4	458	503
2	598	-709
0	438	164
-2	595	868
-4	693	658
-6	119	-115
-8	295	199
-12	98	146
-16	47	-58
-18	39	-99

0,10,L

1	35	49
0	60	49

0,8,L

10	40	-26
5	31	73
1	28	14

0,7,L

8	29	37
4	73	-10
3	42	-44

0,6,L

10	32	63
9	98	41
8	27	9
5	78	11
4	48	-48
3	29	-88
2	29	-18

0,5,L

11	68	-76
10	51	-83
9	32	-42
8	47	-27
7	27	8
6	27	-46
5	36	99
4	65	-53
3	191	229
1	29	-48

0,4,L

15	31	-23
11	46	-19
10	77	-177
9	118	-132
8	189	-178
6	284	248
5	245	-188
4	188	235
3	34	-2
2	91	-14
1	38	28
0	73	-38

0,3,L

15	35	-28
14	52	-68
13	65	-56
12	36	42
11	42	186
10	118	188
9	39	118
7	73	38
5	328	-371
4	291	262
3	281	-535
2	162	42
1	346	184

0,2,L

16	84	189
15	58	86
14	185	127
12	69	67
11	110	187
8	43	184
7	34	-47
6	331	-378
5	74	-33
4	284	267
3	398	449
2	648	-473
1	386	-162
0	698	-887

0,1,L

16	32	-43
13	64	59
12	73	184
11	24	-57
10	89	-81
8	123	211
7	64	-4
6	56	88
5	69	268
4	253	-212
3	347	344
2	423	449
1	482	-72

0,0,L

14	386	-426
12	58	9
10	33	91
8	243	-428
6	62	-134
2	258	44

Table 6.2.4.

Bond lengths (Å) with standard deviations in parentheses.

N(1) - O(1)	1.249(10)	C(6) - C(7)	1.515(9)
N(1) - C(2)	1.434(9)	C(7) - C(8)	1.478(9)
C(1) - C(2)	1.377(9)	C(8) - C(9)	1.499(11)
C(2) - C(3)	1.393(9)	C(9) - N(2)	1.465(8)
C(3) - C(4)	1.378(8)	N(2) - C(5)	1.350(6)
C(4) - C(5)	1.427(8)	N(2) - C(10)	1.468(8)
C(5) - C(6)	1.420(7)	C(10)- C(11)	1.400(14)
C(6) - C(1)	1.343(7)	C(11)- C(12)	1.477(13)
		C(12) - C(4)	1.506(11)
C(1) - H(1)	0.96(6)	C(9) - H(8)	0.81(6)
C(3) - H(2)	0.87(6)	C(10) - H(9)	0.95(6)
C(7) - H(3)	1.05(6)	C(10) - H(10)	1.04(6)
C(7) - H(4)	0.92(7)	C(11) - H(11)	1.16(6)
C(8) - H(5)	1.00(6)	C(11) - H(12)	0.87(6)
C(8) - H(6)	1.07(6)	C(12) - H(13)	0.78(7)
C(9) - H(7)	1.15(6)	C(12) - H(14)	0.92(6)

Table 6.2.5

Bond angles (degrees) with standard deviations in parentheses.

C(2) - N(1) - O(1)	112.6(0.7)	C(7) - C(8) - C(9)	109.9(0.6)
C(1) - C(2) - N(1)	113.4(0.6)	C(8) - C(9) - N(2)	112.3(0.5)
C(3) - C(2) - N(1)	128.4(0.6)	C(9) - N(2) - C(5)	121.8(0.5)
C(1) - C(2) - C(3)	118.1(0.5)	C(9) - N(2) - C(10)	116.0(0.5)
C(2) - C(3) - C(4)	121.5(0.5)	N(2) - C(5) - C(6)	120.2(0.5)
C(3) - C(4) - C(5)	119.0(0.5)	N(2) - C(5) - C(4)	121.2(0.5)
C(4) - C(5) - C(6)	118.7(0.4)	N(2) - C(10) - C(11)	115.2(0.6)
C(5) - C(6) - C(1)	119.3(0.5)	C(10) - N(2) - C(5)	122.0(0.5)
C(6) - C(1) - C(2)	123.4(0.5)	C(10) - C(11) - C(12)	115.6(0.9)
C(1) - C(6) - C(7)	121.4(0.5)	C(11) - C(12) - C(4)	113.0(0.8)
C(5) - C(6) - C(7)	119.3(0.4)	C(12) - C(4) - C(3)	123.6(0.6)
C(6) - C(7) - C(8)	112.3(0.6)	C(12) - C(4) - C(5)	117.4(0.5)

C(2) - C(1) - H(1)	116(3)	C(2) - C(3) - H(2)	124(4)
C(6) - C(1) - H(1)	120(4)	C(4) - C(3) - H(2)	115(4)
C(6) - C(7) - H(3)	106(3)	C(7) - C(8) - H(5)	104(3)
C(6) - C(7) - H(4)	108(4)	C(7) - C(8) - H(6)	114(3)
C(8) - C(7) - H(3)	113(3)	C(9) - C(8) - H(5)	112(3)
C(8) - C(7) - H(4)	117(3)	C(9) - C(8) - H(6)	105(3)
H(3) - C(7) - H(4)	100(5)	H(5) - C(8) - H(6)	112(5)
C(8) - C(9) - H(7)	106(3)	N(2) - C(10) - H(9)	100(4)

Table 6.2.5. (cont'd)

C(8)	- C(9)	- H(8)	114(5)	N(2)	- C(10)	- N(10)	113(4)
N(2)	- C(9)	- H(7)	114(3)	C(11)	- C(10)	- H(9)	117(4)
N(2)	- C(9)	- H(8)	111(5)	C(11)	- C(10)	- H(10)	114(4)
H(7)	- C(9)	- H(8)	99(5)	H(9)	- C(10)	- H(10)	96(5)
C(10)	- C(11)	- H(11)	109(3)	C(11)	- C(12)	- H(13)	116(4)
C(10)	- C(11)	- H(12)	108(4)	C(11)	- C(12)	- H(14)	123(4)
C(12)	- C(11)	- H(11)	110(3)	C(4)	- C(12)	- H(13)	103(5)
C(12)	- C(11)	- H(12)	100(4)	C(4)	- C(12)	- H(14)	107(4)
H(11)	- C(11)	- H(12)	114(5)	H(13)	- C(12)	- H(14)	91(6)

Table 6.2.6.

Torsion angles* (degrees) in the saturated rings.

Atom A	Atom B	Atom C	Atom D	Angle
C(1)	C(6)	C(7)	C(8)	-155.7
C(6)	C(7)	C(8)	C(9)	-51.4
C(7)	C(8)	C(9)	N(2)	53.7
C(8)	C(9)	N(2)	C(10)	155.9
C(9)	N(2)	C(10)	C(11)	156.4
N(2)	C(10)	C(11)	C(12)	41.4
C(10)	C(11)	C(12)	C(4)	-45.8
C(11)	C(12)	C(4)	C(3)	-154.7

*The angle A-B-C-D is defined as positive if when viewed along the B-C bond atom A has to be rotated clockwise to eclipse atom D.

Table 6.2.7.

Displacements (Δ) of atoms from mean plane through aromatic ring.

Equation of plane :

$$0.3540X' + 0.8348Y' - 0.4216Z' = 2.0802 \text{ Å}$$

where X', Y' and Z' are absolute orthogonal co-ordinates (in Å, with $X' = \underline{a}x\sin\beta$, $Y' = \underline{b}y$, and $Z' = \underline{c}z\cos\beta + \underline{a}x$).

Atoms in plane	Δ(Å)
C(1)	-0.010
C(2)	0.004
C(3)	0.008
C(4)	-0.013
C(5)	0.008
C(6)	0.004
Atoms out of plane	
N(1)	0.064
O(1)	0.183
C(7)	0.070
C(8)	-0.488
C(9)	0.141
N(2)	0.029
C(10)	0.090
C(11)	0.477
C(12)	-0.068

Table 6.2.8.

Some important intermolecular contacts involving the nitroso group. Standard deviations are in parentheses.

Molecular positions other than x, y, z required to describe these contacts are :

I -x, 2-y, 1-z

II -x, 1-y, 1-z

III 1-x, 2-y, 1-z

Atom 1	Atom 2	Contact distance (Å)
O(1)	$C(9)^{I}$	3.57(1)
N(1)	$C(11)^{I}$	3.55(2)
N(1)	$C(8)^{II}$	3.58(1)
C(3)	$O(15)^{III}$	3.45(1)
O(1')	$C(10)^{I}$	3.5(3)
O(1')	$C(11)^{I}$	3.4(3)
O(1)	$H(7)^{I}$	2.7(6)
N(1)	$H(12)^{I}$	2.8(6)
O(1')	$C(8)^{I}$	3.5(3)

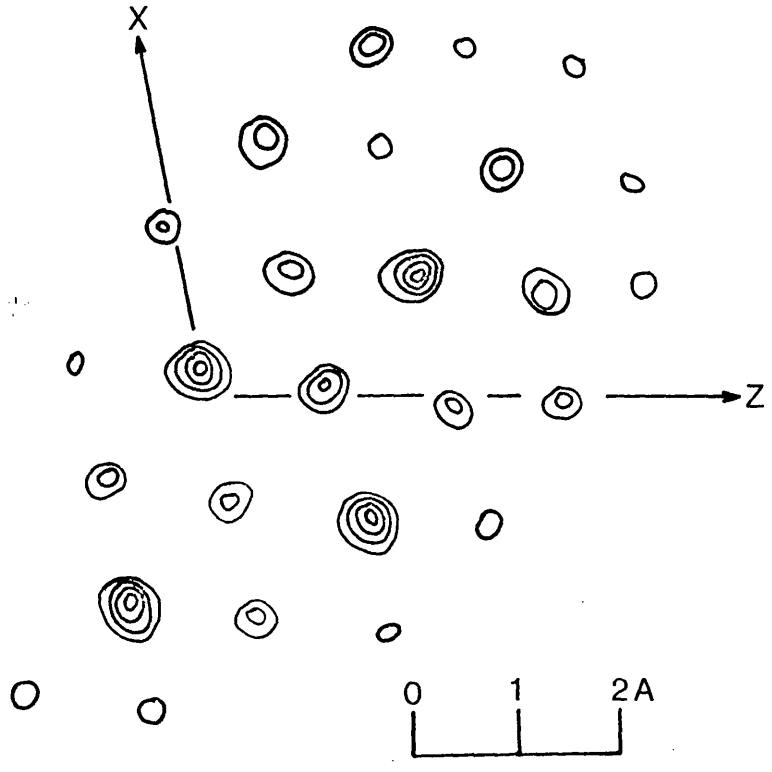


Figure 6.2.1 : The E-map of 9-nitroso julolidine obtained from the symbolic-addition solution.

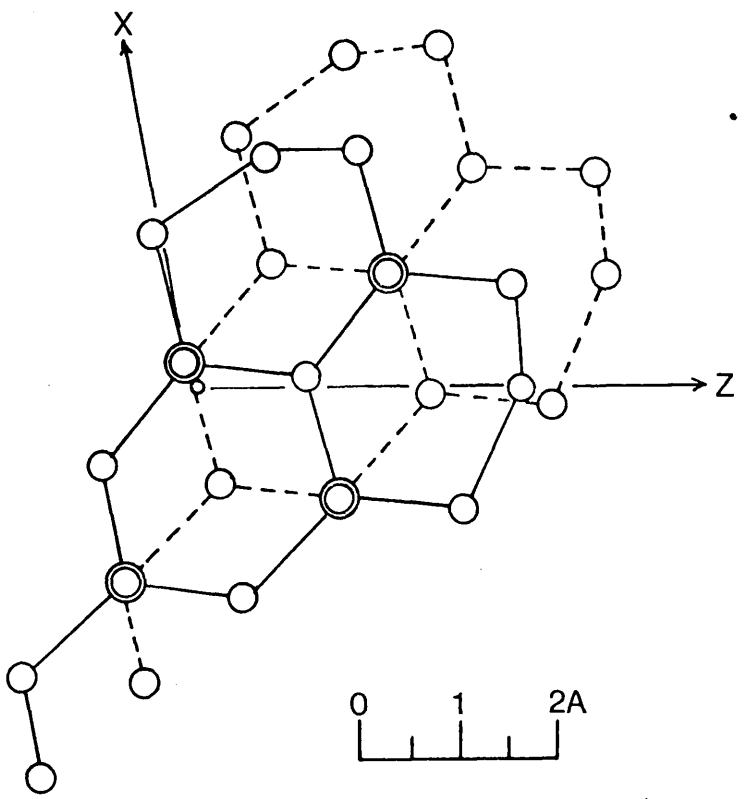


Figure 6.2.2 : The two overlapping half-weight 9-nitroso julolidine molecules proposed as an explanation of the distribution and height of the E-map peaks in Figure 6.1.1.

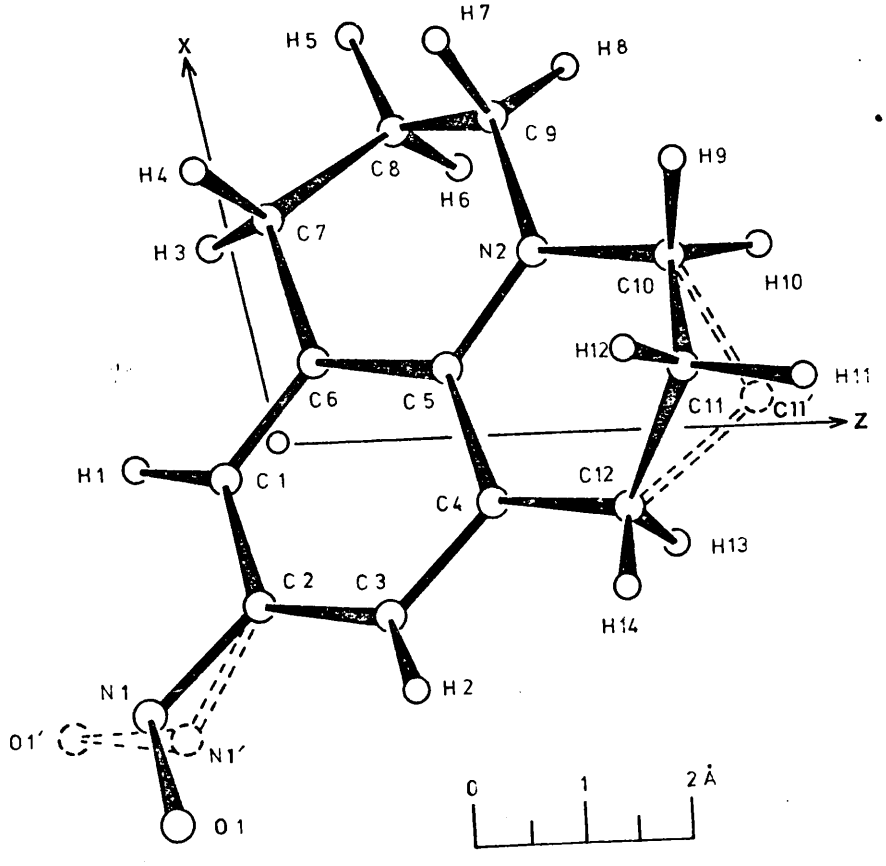


Figure 6.2.3 : The 9-nitroso julolidine molecule projected along the b axis.

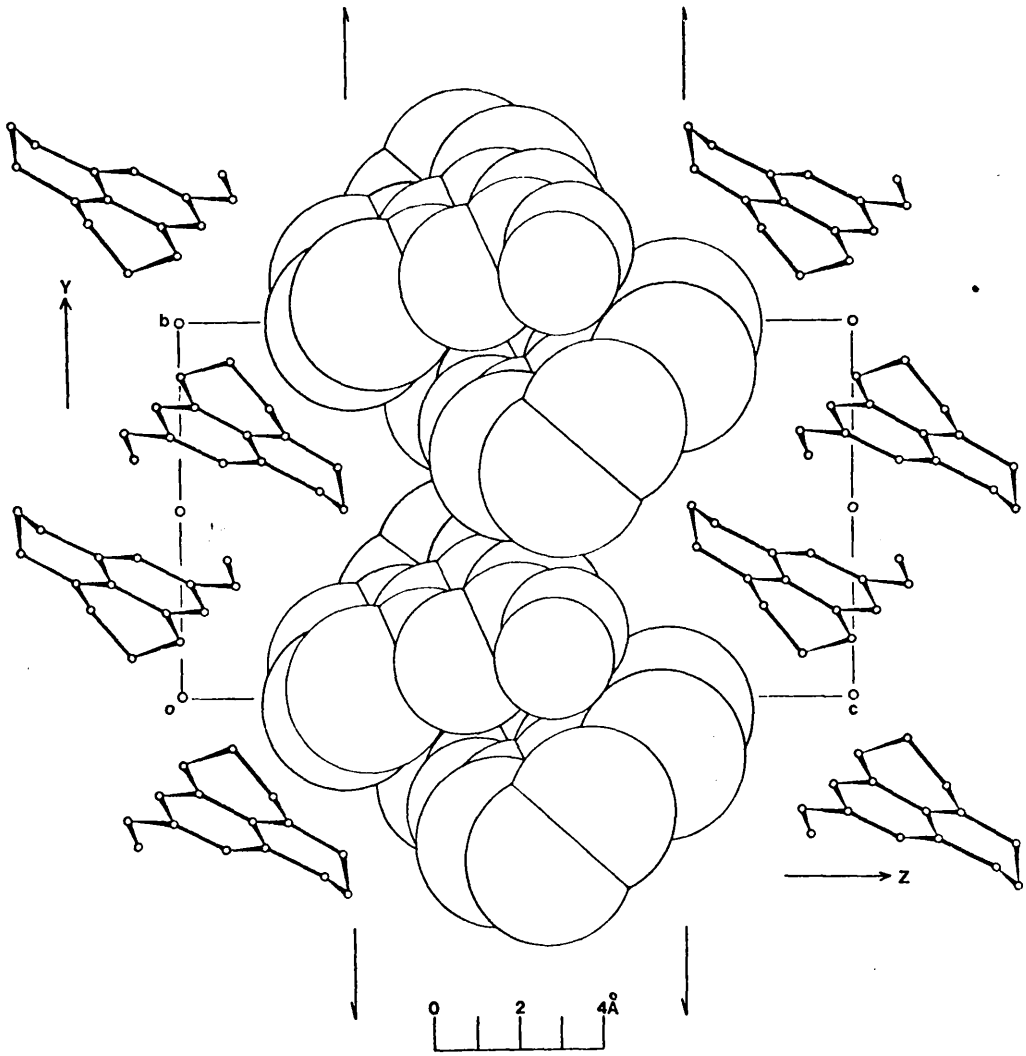


Figure 6.2.4 : The crystal structure of 9-nitroso julolidine projected along a*, showing the head-to-tail molecular pairs. The projection is referred to a left-hand set of axes.

6.3. The Crystal and Molecular Structure of N,N diethyl p-nitroso aniline

6.3.1. Introduction

N,N-diethyl-p-nitrosoaniline was chosen from a number of possible N,N-dialkyl-p-nitrosoanilines as the next p-nitrosoaniline derivative to be studied mainly because of the high quality of its crystals. It was also hoped that the bulky ethyl groups would discourage the formation of the head-to-tail molecular pairs which were thought to be the cause of the disordered nitroso group in 9-nitrosojulolidine.

6.3.2. Experimental

Crystal Data

$C_{20}H_{28}N_4O_2$, M = 356.47. Monoclinic, $\underline{a}$ = 14.717(8), $\underline{b}$ = 10.056(5), $\underline{c}$ = 13.640(6), β = 87.7(0.1)°. $\underline{U}$ = 2,016.97 Å^3, $\underline{D}_m$ = 1.17, $\underline{z}$ = 4, $\underline{D}_c$ = 1.173, $\mu(MoK_\alpha)$ = 0.83 cm^{-1}. Space group $P2_1/n$ (No. 14).

Data Collection

N,N-diethyl-p-nitrosoaniline forms green, prismatic crystals, with the prism axis along $\underline{b}$. The crystal used in the data collection was a prism of dimensions 0.90 x 0.75 x 0.75 m.m^3, which was mounted along its prism axis. The space group and initial cell dimensions were obtained from rotation, Weissenberg and precession photographs, while more accurate cell dimensions were obtained from a least-squares

treatment of 12 high-order reflections whose θ values had been measured automatically on a P.D.P. 8 - controlled four-circle diffractometer. Integrated intensities were measured on the diffractometer for some 300 reflections out to $\theta = 25^{\circ}$, of which 2,160 $|F| > 3\sigma(|F|)$ were used in the subsequent analysis. No absorption corrections were applied to the data.

6.3.3. Structure Analysis and Refinement

The structure was solved by the symbolic addition method, using the 318 reflections with E-values calculated by DATFIX to be greater than 1.3. An origin was defined by assigning positive phases to the reflections 12 4 $\bar{3}$, 4 5 $\bar{11}$, 11 1 $\bar{9}$, and a solution was obtained using the programs SIGMA2 and PHASE. However, the solution was not unique, the phases of the large number of reflections having been determined in terms of the symbolic phase 0 8 1. Two E-maps had to be calculated, corresponding to the two solutions in which the reflection 0 8 1 has respectively a positive and negative phase. Each E-map showed essentially the same features - two unique sets of peaks in planes approximately normal to each other, corresponding to the two N,N-diethyl-p-nitroso-aniline molecules in the asymmetric unit, each set of peaks being interpretable in terms of two overlapping half-weight molecular images - the same effect as was found with 9-nitrosojulolidine. The co-ordinates of each of the two pairs of half molecules in both E-maps were averaged, and structure factors were calculated from these 'averaged' co-ordinates. The structure factors based on the co-ordinates obtained from the first

E-map (corresponding to the solution in which the phase of 0 8 1 = +1) gave an R-value of 66 per cent, while those based on the co-ordinates obtained from the second E-map (corresponding to the solution in which the phase of 0 8 1 = -1) gave an R-value of 44 per cent and this latter solution was subsequently proved by refinement to be the correct one.

Three cycles of full-matrix isotropic least-squares reduced R from 44 per cent to 20 per cent, and a difference map calculated at this stage revealed all the hydrogen atoms and also showed that the nitroso groups of both molecules were disordered, and by different amounts. In the subsequent four cycles of refinement, all of the non-hydrogen atoms in the N,N-diethylaniline residue except C(1) and C(9) were refined by block diagonal least-squares with anisotropic temperature factors; C(1) and C(9) were refined by full-matrix anisotropic least-squares and the disordered nitroso atoms O(1), O(1'), N(1), O(2), O(2') and N(3) by full-matrix least-squares, with their isotropic temperature factors (U) and population parameters (p) subject to the following constraints :

$$p[O(1)] + p[O(1')] = 1 \qquad U[O(1)] = U[O(1')]$$
$$p[N(1)] = p[O(1)]$$
$$p[O(2)] + p[O(2')] = 1 \qquad U[O(2)] = U[O(2')]$$
$$p[N(2)] = p[O(2)]$$

The co-ordinates of N(1') and N(3') were not refined but their temperature factors and population parameters were assigned the values :

$$U[N(1')] = U[N(1)] \qquad p[N(1')] = p[O(1')]$$
$$U[N(3')] = U[N(3)] \qquad p[N(3')] = p[O(2')]$$

The hydrogen atom co-ordinates only were refined, their temperature factors being fixed at those of their parent carbon atoms at the end of the isotropic refinement. During the final three cycles of least-squares refinement, the following weighting scheme was applied :

$$W = X \times Y$$

If $A \times F_{obs} > |F_{calc}|$, $W = 0.000000001$

If $\sin\theta > B$, $X = 1$, else $X = \sin\theta/B$

If $C > F_{obs}$, $Y = 1$, else $Y = C/F_{obs}$

The final values of A, B and C were 0.3, 0.5 and 8.0 respectively, and the R-value at the end of the refinement was 8.3 per cent.

The atomic co-ordinates and temperature factors are listed in Tables 6.3.1. and 6.3.2. respectively, and the observed structure amplitudes and calculated structure factors are listed in Table 6.3.3.

6.3.4 Description and Discussion of the Structure

The bond lengths and angles of the two N,N-diethyl-p-nitrosoaniline molecules in the asymmetric unit are listed in Tables 6.3.4. and 6.3.5. respectively. The numbers assigned to the atoms of the asymmetric unit are shown in Figure 6.3.1.

The molecular packing as viewed down b is shown in Figure 6.3.2.

Molecules which are symmetrically related to molecule I in Figure 6.3.1. (hereafter referred to as Type I molecules) have their aromatic rings approximately parallel to the 010 plane, while those symmetrically related to molecule II in Figure 6.3.1. (Type II molecules) have their aromatic rings approximately parallel to the 101 plane. Type I and Type II molecules are stacked alternatively on top of each other in the b direction, while in the ac plane, Type I and II molecules alternate along the direction of the n-glide. Also in the ac plane, molecules of each type are arranged head-to-tail in rows parallel to 101. Each molecule of one type is thus surrounded by four molecules of the other type - above, below and on both sides of the aromatic plane - with the result that there are no parallel contacts between aromatic rings, as in 9-nitrosojulolidine, the angle between the mean planes through the aromatic rings of Type I and II molecules being 87 degrees. The molecules of N,N-diethyl-p-nitrosoaniline are thus less densely packed than these of 9-nitrosojulolidine, and this is reflected in the lower calculated density of the former (1.173 compared with 1.323). There are no intermolecular contacts worthy of special mention, all such contacts corresponding to normal van der Waals distances. C $\cdots$ C contacts less than 3.80 Å, and C $\cdots$ O contacts less than 3.60 Å are listed in Table 6.3.6. In particular, there are no contacts sufficiently close to either of the nitroso groups to force them to adopt exclusively one or other of their two possible orientations (in the planes of the aromatic rings). The nitroso groups of both molecules in the asymmetric

unit are thus disordered, the relative populations of the two orientations being 83:17 in molecule I and 76:24 in molecule II. The greater disorder of the molecule II nitroso group is reflected in the higher standard deviations of its dimensions. The dimensions of the molecule I nitroso group (C-N = 1.432(9) Å, N-O = 1.231(8) Å, ∠C-N-O = 111.3 (0.6)°) are in good agreement with the dimensions of the nitroso group in 9-nitrosojulolidine, but the dimensions of the molecule II nitroso group (C-N = 1.463(10) Å, N-O = 1.185(11) Å, ∠C-N-O = 109.9(0.8)°) differ significantly from those of both the molecule I and 9-nitroso-julolidine nitroso groups. It seems likely, therefore, that the standard deviations of the molecule II nitroso atomic positions, as determined from the least-squares residuals, are over-optimistic.

The bond lengths of the two N,N-diethylaniline residues are strongly suggestive of a quinonoid-type structure, but the differences in the bond-lengths of the aromatic rings in each residue are not significant on the basis of the estimated standard deviations. If, however, chemically equivalent bonds in both residues are averaged, the differences in the mean bond lengths thus obtained are significant. These mean bond lengths are shown in Figure 6.3.3. together with the mean bond angles; the C(4)-N(2) bond length of 1.349(4) Å, which is the same as the equivalent bonds in N,N-dimethyl-p-nitroaniline and 9-nitrosojulolidine, and the C(2)-C(3) bond lengths of 1.374(4) Å, which is significantly shorter than the C-C length in benzene, confirm a quinonoid-type structure. The bond at the amino end of the aromatic ring, C(3)-C(4), is significantly longer at 1.413(3) Å than the other

ring bonds, a feature also found in 9-nitrosojulolidine, N,N-dimethyl-p-nitroaniline and p-nitroaniline. The N(2)-C(7) distances of 1.466(3) Å compares with the normal C-N single-bond length of 1.47 Å, but the C(7)-C(8) distance of 1.508(4) Å is significantly shorter than the normal C-C single-bond length of 1.54 Å. This 'apparent' shortening of the ethyl group C-C bonds (there can be no chemical explanation for it) must be due to the rather large vibrational amplitudes of the terminal methyl groups. The conformation of the diethylamino group is the same in both molecules of the asymmetric unit, one C-C bond pointing upwards, the other downwards, with an average torsion angle about the C-N bond of 87°. The individual torsion angles are listed in Table 6.3.7. The average C-H distance in the ethyl groups is 0.98 Å, with a root mean square deviation of 0.07 Å, and the average aromatic C-H distance is 0.95 Å with a root mean square deviation of 0.08 Å.

The mean planes of the aromatic ring, amino group and nitroso group of both molecules are listed in Table 6.3.7, together with the deviations of the atoms from the planes, and the angles between the planes. The aromatic rings of both molecules I and II are planar within the limits of experimental error, but the diethyl amino groups are twisted out of the aromatic planes about the C-N bonds by 6.0° and 2.4° respectively. The nitroso group of molecule I is coplanar with the aromatic ring, but that of molecule II is twisted out of the plane by 5.3°. Since the two molecules can be resonably assumed to be chemically identical, these differences in the orientations of the diethylamino and nitroso groups must be due to crystal packing forces,

although the significance of the molecule II nitroso group - aromatic ring angle of 5.3° must be considered doubtful, since the estimated standard deviations of the nitroso group nitrogen and oxygen positions are thought to be too low.

Both of the amino groups are planar within experimental error, although the displacements in Table 6.3.8. suggest they are slightly pyramidal.

6.4. Conclusion

The structure analyses of 9-nitrosojulolidine and N,N-diethyl-nitrosoaniline have provided the structural details which confirm the large contribution of the quinonoid structure II (Section 6.1.) to the electronic structure of p-nitrosoanilines predicted by their physical and spectroscopic properties. The amino and nitroso groups have been shown to be more or less coplanar with the aromatic ring, and the dimensions of the aromatic ring have been shown to be significantly altered by the concerted effects of the electron-releasing amino and electron-withdrawing nitroso substituents. In addition, the dimensions of a monomeric aromatic nitroso group have been established with reasonable accuracy; **the mean values of the dimensions of the 9-nitroso julolidine and the molecule I N,N-diethyl p-nitrosoaniline nitroso groups** (which are disordered to exactly the same extent) are : C-N = 1.433(6) $\mathring{A}$; N-O = 1.240(6) $\mathring{A}$ and $\angle CNO = 112.0(0.7)^{\circ}$. These values appear to be more chemically acceptable than those determined for p-iodonitrosobenzene, for which a similar quinonoid structure is postulated, of 1.28 $\mathring{A}$ for C-N, 1.24 $\mathring{A}$ for N-O and 125° for $\angle CNO$.

References.

1. M.S.Webster, J.Chem.Soc., 2841 (1956).

2. M.I.Davis, J.E.Boggs, D.Caffey Jr. and H.P.Hanson, J.Phys.Chem., 69, 3729 (1965).

3. G.R.Bird, J.Chem.Phys., 25,1040 (1956).

4. Baeyer and Caro, Ber., 7, 809 (1874)

5. B.G.Gowenlock and W.Luttke, Quart.Rev., 12, 321(1958).

6. R.Dunlop, R.K.Mackenzie, D.D.MacNicol, H.H.Mills and D.A.R.Williams, Chem.Comm,919 (1971).

7. H.B.Burgi and J.D.Dunitz, Acta. Cryst., Sect. A, 27, 117 (1971).

8. T.C.Mak and J.Trotter, Acta Cryst., 18, 68 (1965).

9. K.N.Trueblood, E.Goldish and J.Donohue, Acta Cryst., 14, 1009 (1961).

TABLES AND DIAGRAMS

Table 6.3.1.

Fractional co-ordinates (x, y, z) with population parameters (p) other than unity. Standard deviations are in parentheses.

	x	y	z	p
O(1)	0.3106(4)	0.3179(6)	0.5579(4)	0.83(2)
O(1')	0.2339(29)	0.2944(36)	0.4621(26)	0.17(2)
N(1)	0.2912(5)	0.2990(6)	0.4704(5)	0.83(2)
N(1')	0.3080	0.3000	0.4900	0.17(2)
N(2)	0.5813(3)	0.2908(4)	0.2194(2)	
C(1)	0.3710(3)	0.2984(4)	0.4136(3)	
C(2)	0.3519(3)	0.2782(5)	0.3135(4)	
C(3)	0.4222(3)	0.2751(4)	0.2498(3)	
C(4)	0.5123(3)	0.2939(4)	0.2816(3)	
C(5)	0.5305(3)	0.3153(4)	0.3841(3)	
C(6)	0.4592(4)	0.3184(4)	0.4464(3)	
C(7)	0.6768(4)	0.2973(5)	0.2531(4)	
C(8)	0.7104(4)	0.4394(7)	0.2676(5)	
C(9)	0.5648(4)	0.2799(5)	0.1123(3)	
C(10)	0.5608(5)	0.1377(5)	0.0781(3)	
O(2)	0.3893(5)	0.2084(8)	-0.0866(5)	0.76(2)
O(2')	0.3889(14)	0.3765(21)	-0.0859(14)	0.24(2)
N(3)	0.3583(5)	0.3115(9)	-0.0627(5)	0.76(2)
N(3')	0.3550	0.2680	-0.064	0.24(2)

Table 6.3.1. (cont'd)

	x	y	z
N(4)	0.0721(3)	0.2778(3)	0.1946(2)
C(11)	0.2841(3)	0.2890(6)	0.0036(3)
C(12)	0.2412(3)	0.4036(5)	0.0298(3)
C(13)	0.1703(3)	0.4015(4)	0.0915(3)
C(14)	0.167(3)	0.2801(4)	0.1337(3)
C(15)	0.1875(3)	0.1630(4)	0.1072(3)
C(16)	0.2576(3)	0.1677(5)	0.0437(3)
C(17)	0.0270(4)	0.3998(5)	0.2250(4)
C(18)	-0.0488(4)	0.4422(6)	0.1547(5)
C(19)	0.0388(3)	0.1545(4)	0.2376(3)
C(20)	0.0904(5)	0.1166(5)	0.3304(4)
H(1)	0.295(4)	0.263(6)	0.306(4)
H(2)	0.399(4)	0.259(6)	0.178(4)
H(3)	0.582(4)	0.322(6)	0.401(4)
H(4)	0.479(4)	0.332(6)	0.516(4)
H(5)	0.718(4)	0.246(6)	0.210(5)
H(6)	0.691(4)	0.252(6)	0.321(4)
H(7)	0.768(4)	0.437(7)	0.272(5)
H(8)	0.668(4)	0.485(7)	0.312(5)
H(9)	0.697(4)	0.493(7)	0.207(5)
H(10)	0.515(4)	0.332(6)	0.094(4)
H(11)	0.616(4)	0.321(6)	0.085(4)

Table 6.3.1. (cont'd)

	x	y	z
H(12)	0.500(4)	0.092(7)	0.103(5)
H(13)	0.551(4)	0.141(7)	0.002(5)
H(14)	0.605(4)	0.089(7)	0.097(5)
H(15)	0.272(4)	0.489(6)	0.010(4)
H(16)	0.135(4)	0.484(5)	0.102(4)
H(17)	0.167(4)	0.077(6)	0.132(4)
H(18)	0.287(4)	0.088(5)	0.032(4)
H(19)	0.993(4)	0.380(6)	0.275(4)
H(20)	0.076(4)	0.471(6)	0.240(4)
H(21)	0.965(4)	0.458(7)	0.085(5)
H(22)	0.909(5)	0.373(7)	0.147(5)
H(23)	0.909(4)	0.518(7)	0.179(5)
H(24)	0.978(4)	0.163(6)	0.249(4)
H(25)	0.039(4)	0.084(6)	0.188(4)
H(26)	0.104(5)	0.178(7)	0.379(5)
H(27)	0.163(4)	0.091(7)	0.312(5)
H(28)	0.053(4)	0.047(7)	0.356(5)

Table 6.3.2.

Vibrational parameters ($\mathring{A}^2$) with standard deviations in parentheses.

	U_{11} or U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	0.105(3)					
O(1')	0.105					
N(1)	0.092(2)					
N(1')	0.092					
N(2)	0.074(2)	0.062(2)	0.047(2)	-0.002(2)	0.010(2)	-0.002(1)
C(1)	0.066(3)	0.057(2)	0.071(3)	0.002(2)	-0.021(2)	0.002(2)
C(2)	0.062(2)	0.063(3)	0.081(3)	-0.003(2)	0.005(2)	0.002(2)
C(3)	0.074(3)	0.055(2)	0.057(2)	-0.003(2)	-0.001(2)	0.001(2)
C(4)	0.065(2)	0.044(2)	0.044(2)	-0.001(2)	0.003(2)	0.002(2)
C(5)	0.059(2)	0.066(2)	0.047(2)	0.005(2)	-0.001(2)	0.004(2)
C(6)	0.097(3)	0.057(2)	0.046(2)	0.005(2)	0.013(2)	0.001(2)
C(7)	0.076(3)	0.079(3)	0.070(3)	0.006(2)	0.021(2)	-0.003(2)
C(8)	0.098(4)	0.095(4)	0.100(4)	-0.027(3)	0.022(3)	-0.004(3)
C(9)	0.098(3)	0.064(3)	0.042(2)	-0.008(2)	0.008(2)	0.002(2)
C(10)	0.136(5)	0.066(3)	0.053(2)	0.001(3)	0.013(3)	0.008(2)
O(2)	0.123(4)					
O(2')	0.123					
N(3)	0.100(2)					
N(3')	0.100					

Table 6.3.2. (cont'd)

	U_{11} or U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(4)	0.079(2)	0.043(2)	0.057(2)	-0.004(2)	0.019(2)	-0.005(1)
C(11)	0.056(2)	0.107(4)	0.046(2)	-0.012(2)	0.007(2)	0.001(2)
C(12)	0.071(3)	0.082(3)	0.059(2)	-0.012(2)	0.006(2)	0.007(2)
C(13)	0.072(3)	0.055(2)	0.062(2)	-0.010(2)	0.014(2)	0.001(2)
C(14)	0.058(2)	0.053(2)	0.044(2)	-0.004(2)	0.007(2)	-0.005(2)
C(15)	0.065(2)	0.059(2)	0.053(2)	0.002(2)	0.002(2)	-0.008(2)
C(16)	0.068(3)	0.085(3)	0.057(2)	0.013(2)	-0.002(2)	-0.019(2)
C(17)	0.104(4)	0.056(3)	0.076(3)	-0.003(2)	0.038(3)	-0.012(2)
C(18)	0.102(4)	0.069(3)	0.123(5)	0.017(3)	0.033(4)	-0.003(3)
C(19)	0.082(3)	0.054(2)	0.065(2)	-0.017(2)	0.020(2)	-0.001(2)
C(20)	0.145(5)	0.072(3)	0.060(3)	-0.021(3)	0.014(3)	0.007(2)
H(1)	0.07					
H(2)	0.06					
H(3)	0.06					
H(4)	0.07					
H(5)	0.08					
H(6)	0.08					
H(7)	0.10					
H(8)	0.10					
H(9)	0.10					
H(10)	0.07					
H(11)	0.07					

Table 6.3.2. (cont'd)

	U_{iso}
H(12)	0.08
H(13)	0.08
H(14)	0.08
H(15)	0.07
H(16)	0.06
H(17)	0.06
H(18)	0.07
H(19)	0.08
H(20)	0.08
H(21)	0.10
H(22)	0.10
H(23)	0.10
H(24)	0.07
H(25)	0.07
H(26)	0.09
H(27)	0.09
H(28)	0.09

Table 6.3.3

Observed structure amplitudes and final calculated structure factors. (×10)

17,2,L

2	25	-19
-3	29	-32

17,1,L

0	41	-26

17,0,L

-3	42	49

16,4,L

3	52	42
2	58	-58
-3	28	-18

16,3,L

4	26	-25
1	28	-27

16,2,L

3	58	-47
2	52	39
1	28	-26
-2	26	-25
-4	25	28
-5	28	15

16,1,L

4	24	8
2	32	-26
1	27	21
-2	72	56
-3	31	27
-4	62	38

16,0,L

6	26	-24
-2	46	49
-4	61	-61

15,6,L

1	39	38
0	28	26

15,5,L

4	33	27
-1	28	-30

15,4,L

2	29	-25
0	41	-39
-1	54	54

15,3,L

3	41	32
2	51	-49
1	63	54
-2	31	-15
-3	24	18

15,2,L

3	26	-6
0	32	23
-1	48	-42
-3	28	28
-4	24	26
-7	28	6

15,1,L

7	28	-23
3	41	-33
2	36	33
0	30	26
-1	27	-22
-4	34	23
-7	25	5

15,0,L

5	66	54
3	23	12
-3	42	-38
-5	35	-26

14,7,L

-1	34	25

14,6,L

2	60	53
0	67	-60
-1	75	-78
-4	27	-18

14,5,L

5	26	20
2	29	-25
1	63	-58
-1	94	-84

14,4,L

4	34	23
0	131	124
-1	97	96

14,3,L

7	24	21
6	34	-29
5	50	-46
3	24	-26
2	39	32
-1	125	108
-2	55	-58
-4	30	24
-5	40	36
-7	32	-23
-8	29	17

14,2,L

6	35	-26
4	48	-47
3	48	-36
2	36	-29
1	50	48
0	89	-87
-2	67	67
-3	23	19
-6	60	-63

14,1,L

6	58	65
5	28	29
3	26	26
0	58	-54
-1	42	-44
-3	34	-31
-4	48	-42
-6	39	-25

14,0,L

8	26	-10
6	27	30
4	61	66
0	32	29
-2	83	-76
-6	101	98
-10	29	53

13,8,L

-1	44	41

13,7,L

4	47	-46
0	31	-34
-2	79	75

13,6,L

4	37	-37
1	43	-46
0	104	-98
-1	91	-85
-7	36	31

13,5,L

8	33	-21
4	41	46
-1	38	31
-2	32	-24
-3	31	27

13,4,L

6	48	-33
5	25	24
4	54	45
3	24	-19
2	25	-19
1	85	79
0	208	189
-1	67	-57
-2	26	25
-3	74	-70
-6	25	-25
-7	24	-20

13,3,L

8	36	29
6	24	-28
5	28	-32
4	37	-50
2	27	25
1	53	-53
0	57	66
-1	26	-24
-2	87	80
-3	49	-43
-7	35	-29
-8	26	-28

13,2,L

6	30	22
5	36	-44
3	58	75
1	44	-47
0	63	-64
-1	184	160
-2	50	-47
-3	52	48
-7	40	-34

13,1,L

6	27	26
5	81	83
3	36	-44
0	53	-47
-1	134	-127
-2	88	-76
-3	96	89
-7	129	112

13,0,L

3	69	-76
1	59	-39
-1	135	-121
-5	31	56
-7	58	44
-11	41	27

12,8,L

1	26	-21
0	47	41
-1	53	52
-2	26	26
-3	26	-34
-4	25	-16
-5	35	34

12,7,L

3	37	34
0	54	-42
-1	30	34
-3	28	-31
-4	27	24
-6	26	22
-7	42	-47

12,6,L

8	55	-56
-1	54	-54
-2	25	18
-3	180	178
-5	25	-18
-6	33	36
-7	27	30

12,5,L

8	57	46
7	42	33
5	36	37
3	32	-23
-3	73	69
-4	75	-75
-5	23	-8
-7	30	30
-10	28	28

12,4,L

9	46	45
7	28	21
6	43	-39
3	27	43
1	45	-40
-1	98	97
-2	241	-199
-3	313	-309
-4	105	103
-6	51	-45
-7	43	-50
-8	52	57
-9	76	70
-10	38	-42

12,3,L

2	24	26
1	36	40
-1	64	61
-3	91	-79
-4	120	113
-6	27	-37
-7	55	-46

12,2,L

9	48	-39
8	28	28
2	56	55
-1	27	-48
-2	309	296
-3	132	120
-4	147	-137
-6	37	31
-8	28	-33
-7	48	-36
-9	36	-26
-10	24	42

12,1,L

9	24	-23
4	80	-125
3	22	-29
2	38	-47
0	76	-78
-1	76	-64
-2	167	147
-3	32	24
-4	35	37
-6	71	87
-7	61	63
-8	42	-63

12,0,L

8	48	-32

-2	224	-222
-4	96	87
-6	38	-37
-8	43	-41

11,9,L

2	36	-38
1	24	-15
-2	34	-28
-3	52	-50

11,8,L

6	26	16

11,7,L

2	39	41
-2	98	93
-3	77	79
-4	75	-73
-5	33	28
-8	85	-76

11,6,L

0	28	-28
-1	68	62
-5	39	38
-9	26	-15

11,5,L

9	33	25
8	26	11
6	48	-48
5	36	-32
4	39	50
2	34	-35
1	25	28
-1	58	-57
-2	147	-141
-3	109	-110
-6	42	-55
-8	73	67

11,4,L

5	31	43
1	29	38
-1	98	-95
-2	219	-223
-3	127	122
-4	176	-161
-5	93	88
-8	26	23
-10	59	41

11,3,L

11	32	23
8	25	-8
7	86	63
3	35	57
-1	89	88
-2	79	79
-3	37	-26
-4	29	-32
-8	42	-36
-9	58	58
-10	32	50

11,2,L

10	39	-39
3	28	-26
2	58	-65
1	62	-75
0	48	-48
-1	37	34
-2	141	144
-3	113	-109
-4	142	131
-5	104	-97
-6	49	52
-9	26	-24
-12	25	-15

11,1,L

11	58	-38
9	42	-31
7	23	-38
4	23	-44
3	69	-86
2	26	-19
1	73	63
-2	54	38
-1	58	-35
-2	21	-9
-3	339	311
-4	48	48
-5	32	-43
-6	22	24
-7	54	45
-9	235	-229
-10	47	-61
-12	29	18

11,0,L

11	53	44
9	28	26
3	183	178
1	125	121
-1	97	-93
-3	135	130
-5	22	-23
-7	49	-59
-9	41	36

10,9,L

-3	68	62
-4	26	-29

10,8,L

1	55	55
-3	31	-29
-4	88	-79
-7	39	-37

10,7,L

3	59	58
2	27	-28
-1	73	-77
-2	37	43
-3	23	-28
-4	88	92
-5	26	21
-9	59	53

10,6,L

10	45	42
9	48	-39
8	24	23
4	42	-43
-3	87	85
-4	47	-41
-6	45	45
-9	71	-72

10,5,L

10	58	43
8	24	-12
7	44	-43
5	73	-90
1	68	-68
-1	98	91
-2	72	-77
-3	93	-95
-5	30	32
-6	84	79

10,4,L

9	45	35
4	27	33
0	30	29
-2	31	37
-3	68	-66
-4	223	231
-5	283	293
-6	135	-130
-7	38	37

Table 6.3.3 (cont'd)

12,4,L

	89	96
-10	54	-58
-11	36	-44

10,3,L

10	59	-56
9	55	-51
6	32	38
5	55	93
4	37	-77
3	27	-45
2	55	56
0	118	-126
-1	28	-33
-2	35	-34
-3	38	39
-4	110	-107
-5	38	-39
-6	98	-93
-11	25	19
-12	33	17

10,2,L

12	52	-43
11	33	-33
10	88	-79
9	46	-35
5	23	54
4	22	28
2	54	-47
-2	26	-20
-3	176	178
-4	190	-196
-5	153	-148
-6	42	29
-7	33	33
-8	62	-71
-9	41	-46
-10	35	40

10,1,L

10	120	113
9	58	47
8	31	-36
3	20	-2
2	118	131
1	76	74
0	245	208
-1	33	39
-2	53	72
-8	78	-100
-11	30	-35

10,0,L

12	79	67
10	113	103
8	24	-47
2	36	-1
0	107	-96
-2	103	-102
-4	208	205
-8	117	141
-10	23	24
-12	27	-35

9,9,L

3	37	-32
2	23	18
-5	26	28
-6	31	-34

9,8,L

7	31	27
5	25	16
1	38	30
0	64	-61
-5	49	-52

9,7,L

7	27	24
1	25	13
0	40	-43
-2	41	41
-6	28	-22
-10	57	48

9,6,L

8	62	-53
7	36	-32
6	42	-46
5	74	-72
-3	82	-86
-4	104	-105
-5	66	71
-6	68	-66
-7	39	39
-8	32	47
-10	25	-22

9,5,L

10	87	74
9	37	-43
8	37	-32
5	40	49
2	26	25
1	49	48
0	65	-63
-3	27	-28
-4	153	144
-5	109	110
-6	225	224
-7	60	-63
-10	28	-16
-12	44	-19

9,4,L

11	43	-32
10	41	-38
9	60	49
8	37	51
6	34	41
5	47	56
4	75	113
3	74	-86
0	31	28
-3	70	55
-4	150	158
-5	231	-224
-7	60	-63

9,3,L

12	39	-40
11	84	-72
10	156	-139
8	52	68
7	42	-68
6	36	66
5	51	-90
4	52	85
1	73	83
0	55	51
-1	88	-85
-2	75	-72
-4	114	-109
-5	93	-97
-6	209	-198
-7	150	151
-10	58	48
-11	38	-31
-12	25	-4
-13	26	-21

9,2,L

13	29	-30
10	66	64
7	24	39
4	25	-45
3	36	91
2	39	-54
1	48	63
0	108	84
-1	27	26
-2	18	0
-3	35	-29
-5	112	123
-6	49	-48
-10	66	-71
-11	65	50
-13	26	17

9,1,L

12	51	49
11	163	142
10	91	87
9	31	-42
6	32	-41
3	27	-32
2	27	-18
1	103	-125
0	55	55
-1	192	-192
-6	34	39
-7	37	-35
-9	31	-35
-10	62	-54
-11	136	125

9,0,L

13	49	40
11	44	-24
7	53	-85
5	49	-117
3	36	53
1	299	-289
-1	61	-56
-3	42	41
-5	182	171
-7	25	-30
-9	68	96
-11	101	-86
-13	48	-50

8,10,L

4	25	-18
0	37	39

8,9,L

7	70	-62
5	31	26
3	54	-49
1	77	79
-1	28	-23
-3	30	-28
-4	24	-31
-5	47	-45
-7	33	-26

8,8,L

7	69	-64
6	44	41
5	29	24
4	44	48
2	38	-29
1	27	18
-2	30	27
-4	28	-33
-7	26	29

8,7,L

9	99	-92
7	124	114
6	55	-41
3	68	62
1	78	-76
-1	56	-51
-3	98	106
-5	55	52
-6	33	-33
-10	34	-31
-11	51	-51

8,6,L

11	36	24
9	80	-68
8	43	-34
7	72	68
6	47	-44
5	38	-37
4	35	-28
3	130	122
1	94	-96
-1	64	64
-2	58	-64
-3	69	-69
-4	41	42
-5	62	60
-6	62	64
-7	95	86
-8	33	29
-11	35	33

8,5,L

9	127	115
7	88	-108
6	25	28
5	72	87
4	26	-35
3	25	0
2	74	-71
0	73	76
-1	53	49
-2	103	-87
-3	113	-107
-4	97	87
-5	84	86
-6	77	-75
-8	44	-41
-12	28	-20

8,4,L

11	48	-31
10	31	29
9	118	135
8	59	-66
7	37	-37
5	56	63
4	142	-165
3	160	-161
2	110	98
0	26	-21
-1	61	64
-3	86	76
-4	82	-91
-5	91	-99
-6	124	-130
-7	241	-234
-8	71	65
-9	24	37
-11	86	-74
-12	58	62

8,3,L

10	81	-65
9	49	-64
8	116	157
7	76	107
6	45	-58
5	28	-42
4	35	58
3	26	1
2	28	-26
0	65	56
-1	130	136
-2	150	134
-3	145	152
-5	152	-152
-6	206	212
-7	22	-18
-8	53	58
-10	26	-34
-12	55	60

8,2,L

13	27	26
11	59	58
10	44	-48
9	23	-20
8	104	146
7	25	-25
5	21	-36
4	123	176
3	93	121
2	39	-37
1	31	-42
0	68	75
-1	62	-61
-2	87	-82
-3	49	-53
-4	75	77
-5	40	-37
-6	23	26
-8	117	-108
-9	63	55
-10	77	84
-13	24	18

8,1,L

14	27	16
10	27	-32
8	365	-413
7	34	-41
6	69	81
5	31	-31
4	22	-33
3	30	-35
2	264	251
1	60	-67
0	194	-189
-1	67	-61
-2	418	-398
-3	177	-181
-4	83	-84
-5	63	55
-6	54	51
-7	50	56
-9	28	25
-10	57	60
-12	56	-72

8,0,L

14	29	30
10	46	39
8	126	-116
6	25	44
4	70	-75
2	145	122
0	257	-258
-2	399	337
-6	124	133
-10	58	-72
-12	117	-111
-14	40	63

7,10,L

4	31	-33
3	50	-49
1	35	34
-2	27	-34

7,9,L

8	101	-95
3	50	-48
-2	41	-45
-7	36	-34

7,8,L

9	52	-47
8	26	29
7	48	46
6	27	38
5	24	-14
4	35	35
2	23	-19
0	34	-41
-1	73	72
-2	130	138
-7	34	-28
-8	73	-73

7,7,L

11	27	-11
10	53	-51
9	60	-61
8	158	139
7	83	-85
6	47	-44
4	53	54
3	45	45
2	32	41
1	62	59
0	28	27
-1	29	26
-2	44	47
-5	27	35
-6	48	-44
-7	48	52
-8	27	38
-9	59	-58

7,6,L

12	44	-38
9	35	-32
8	100	-91
7	27	-25
6	29	28
5	46	52
4	33	36
3	60	45
2	241	226
1	26	-21
0	108	-97
-1	38	-39
-2	43	-42
-3	25	-30
-4	39	27
-6	64	78

7,5,L

10	72	67
8	80	-77
7	127	137
6	23	28
5	42	-38
4	75	-82
3	103	-105
2	117	-116
1	67	-60
-1	35	38
-2	144	-151
-3	148	-149
-4	38	28
-5	37	-22
-6	71	-75
-7	42	-51
-8	191	-205
-9	129	135

7,4,L

12	55	49
11	38	-31
9	71	75
8	185	206
7	67	-82
6	102	-95
5	29	26
3	122	-111
2	419	-408
1	214	198
-1	97	-85
-2	48	-38
-3	44	38
-4	78	-67
-5	68	-58
-6	143	-152
-7	217	222
-8	95	83
-9	98	98
-10	137	155
-14	29	-6

7,3,L

11	35	-35
10	38	-24
9	135	145
8	122	135
6	35	11
5	34	36
3	124	128
2	55	-43
1	18	-22
0	24	31
-1	25	-23
-2	89	89
-3	60	-63

Table 6.3.3 (cont'd)

7,3,L

-4	87	79
-5	80	78
-6	103	103
-7	74	76
-8	104	114
-9	183	-182
-10	32	-24
-12	39	-25

7,2,L

13	45	-27
11	26	28
9	146	-151
8	216	-257
6	60	-89
4	26	39
3	151	175
2	200	219
1	173	-155
0	21	-1
-1	37	-36
-2	97	83
-3	148	154
-6	35	42
-7	135	-141
-8	73	-60
-9	138	-141
-10	70	-77
-12	33	7
-13	46	-36
-14	51	44

7,1,L

11	25	7
9	286	-308
8	147	-147
7	143	149
6	42	41
5	108	-136
3	148	190
2	74	77
1	192	187
0	66	-72
-1	291	258
-2	112	97
-3	452	432
-4	148	-137
-5	246	221
-7	117	-100
-8	41	41
-9	41	-44
-13	67	-75
-15	34	45

7,0,L

13	56	42
9	259	246
7	123	137
5	25	33
3	181	-143
1	227	182
-1	83	85
-3	234	-237
-7	105	-97
-9	68	65
-11	52	29
-13	56	43

6,11,L

-1	38	-26

6,10,L

6	48	-48
5	40	-37
3	23	-3
0	31	33
-2	28	-32
-3	39	-46
-4	29	-29

6,9,L

7	26	-28

6 44 -33
5 99 98
3 35 -35
2 39 -41
1 88 85
-1 51 -56
-4 55 -58
-5 77 80

6,8,L

8	35	32
7	55	56
6	46	42
5	55	54
2	49	-48
0	74	-72
-2	95	98
-5	36	-46
-8	48	-44
-9	47	-49

6,7,L

9	24	21
8	64	-63
6	47	48
5	161	-157
4	45	43
3	75	73
2	91	82
1	180	-174
-1	74	80
-3	35	32
-4	64	62
-6	35	34
-8	44	-42
-9	87	-94
-10	31	-27

6,6,L

8	35	32
7	25	-18
6	231	-15
5	41	-37
4	37	42
3	89	64
2	96	-52
1	140	-132
0	98	83
-1	55	57
-2	32	-39
-3	121	132
-4	23	17
-5	55	60
-7	42	-36
-8	48	50
-9	147	-141
-11	29	-27
-13	32	-26

6,5,L

13	32	25
12	53	53
11	38	35
9	49	45
8	36	40
7	191	-201
6	31	-6
4	196	-176
3	142	-124
2	84	79
1	136	124
0	82	75
-2	79	-86
-3	207	-208
-4	49	43
-5	143	134
-6	54	-45
-7	185	-198
-8	142	147
-9	252	260

6,4,L

14	29	31
13	32	36
12	33	-30

11 44 33
10 44 -47
9 67 68
8 94 -94
7 32 -29
6 122 119
5 57 -53
3 74 -61
2 282 264
1 91 74
0 61 -34
-1 62 -73
-2 59 -56
-3 138 -145
-4 28 -26
-5 148 -137
-6 106 99
-7 77 81
-11 50 36
-12 54 52
-13 30 29

6,3,L

14	35	-28
-12	25	27
-14	33	-21

6,2,L

13	26	-30
-2	85	68
-3	291	269
-4	178	165
-5	135	125
-6	68	-59
-7	35	-32
-8	61	-65
-9	79	-68
-10	59	54
-13	57	-54

6,1,L

10	38	-38
8	40	-41
7	46	43
6	576	603
5	189	192
3	195	-232
2	478	531
1	154	147
0	448	-414
-2	286	261
-3	62	57
-4	462	401
-5	76	65
-6	43	50
-7	128	127
-8	73	89
-9	24	17
-10	229	-210
-11	46	-58
-12	40	-39
-13	25	-32
-14	79	73

6,0,L

10	24	15
8	39	23
6	242	-236
4	67	-85
2	192	253
0	149	-118
-2	394	-368
-4	367	-388
-8	59	62
-10	54	56
-12	37	30
-14	40	26

5,11,L

-1	25	-27

5,10,L

7	61	-64
6	26	-25

4 47 48
2 25 -18
1 25 32
-5 37 38

5,9,L

6	164	163
4	38	-25
2	42	34
0	81	-80
-1	39	42
-4	53	53
-6	34	-43
-8	49	-54
-9	34	39

5,8,L

9	42	-35
8	59	59
7	75	77
6	38	-33
5	26	27
4	162	-159
3	59	52
1	89	-86
0	23	16
-1	38	24
-2	87	95
-3	52	-52
-4	128	-127
-5	86	-92
-8	91	-86
-9	25	-31
-10	111	109
-11	51	58

5,7,L

8	25	17
7	50	-49
6	179	-179
5	136	137
2	41	44
1	26	15
0	41	-41
-1	39	-29
-2	41	-43
-3	45	43
-4	100	-103
-6	51	56
-9	71	-71
-11	38	-41

5,6,L

12	24	25
11	34	34
8	49	-53
7	26	-32
6	55	54
5	61	-64
4	92	94
3	44	-31
2	57	53
0	183	-177
-1	116	124
-2	107	-109
-3	64	61
-4	217	216
-6	48	-35
-7	35	38
-10	101	-96
-11	41	-50
-12	55	74
-13	26	-34

5,5,L

12	44	39
11	51	-42
10	61	-54
8	67	-66
7	47	43
6	19	-22
3	42	-36
2	85	84
1	188	191
0	414	398

-1 71 -55
-2 48 45
-4 156 135
-5 128 -116
-6 79 87
-7 118 118
-8 74 82
-9 66 66
-10 153 154
-11 87 -92
-12 49 -59

5,4,L

13	37	-38
12	59	-60
10	32	-47
9	84	83
6	72	-74
5	23	-15
4	28	28
2	74	72
0	172	167
-1	273	-258
-2	58	-41
-3	79	81
-4	148	-135
-7	38	-43
-8	52	47
-9	82	-90
-10	84	83
-11	92	-101
-12	98	-107

5,3,L

13	32	29
12	34	-37
11	72	69
10	43	39
7	52	-55
6	85	94
5	34	-33
4	49	58
3	252	-243
2	330	-341
1	61	-52
0	321	-312
-1	67	58
-2	79	-66
-3	87	-79
-4	130	-108
-5	24	26
-6	64	-63
-7	28	37
-8	113	-125
-9	83	-84
-10	113	-124
-11	239	234
-12	87	95
-14	31	33
-15	37	35

5,2,L

13	34	37
11	35	-38
10	98	99
9	22	-27
8	63	-61
7	238	236
6	175	179
5	338	358
4	191	181
2	25	29
1	201	-243
0	275	-273
-1	244	-231
-2	278	246
-3	79	92
-4	313	303
-5	228	-217
-6	62	-64
-8	64	56
-9	88	-88
-10	137	-133
-11	208	217
-12	35	45
-15	61	64

5,1,L

8	30	27
7	184	186
5	433	-444
4	102	83
2	62	-52
1	264	231
0	168	197
-1	118	93
-2	32	32
-3	48	47
-4	98	91
-5	332	-322
-6	109	-117
-7	149	-156
-8	111	116
-9	84	-98
-10	34	-23
-11	94	-77
-12	36	-46
-15	27	38

5,0,L

15	32	-26
9	54	-47
7	592	-588
5	693	-736
3	34	66
1	736	792
-1	559	548
-3	544	-589
-5	599	603
-7	25	28
-9	289	307
-11	228	-225
-13	27	32
-15	144	-150

4,11,L

0	55	-51
-4	38	29

4,10,L

6	26	25
5	48	46
4	62	66
3	47	-41
1	33	-32
-1	53	51
-3	26	-22

4,9,L

8	33	35
7	69	77
6	37	38
4	38	33
1	33	34
-1	82	-90
-4	38	-25
-5	36	-39
-6	37	38
-7	38	-33
-10	49	49

4,8,L

9	53	-58
5	145	-142
4	38	-16
3	91	91
1	34	24
0	78	-77
-1	28	-26
-2	46	44
-6	87	-93
-7	78	98
-8	25	-26
-11	27	22

4,7,L

10	38	38
9	26	23
8	23	-25

Table 6.3.3 (cont'd)

4,7,L

7	52	-58
6	57	57
4	58	-57
3	76	80
2	58	-63
1	44	-46
-1	108	109
-2	73	-78
-4	49	49
-7	62	61
-8	30	-28
-9	120	-131
-10	40	-37
-11	110	114

4,6,L

12	32	35
11	27	31
10	28	34
9	62	68
8	60	-58
7	98	-97
6	72	-74
5	36	36
4	108	-113
1	57	-58
0	119	117
-1	185	177
-2	21	21
-3	24	22
-4	47	44
-5	32	-41
-6	62	62
-7	140	-154
-8	64	64
-9	62	60
-10	79	-78
-12	67	-65
-13	37	44

4,5,L

11	29	-29
10	68	-67
9	55	-51
8	22	26
7	22	-16
6	46	-44
5	47	-44
4	67	62
3	112	106
2	46	-38
1	275	258
0	137	140
-1	65	-54
-2	128	-123
-3	76	-62
-4	53	56
-5	275	284
-6	118	-129
-7	64	-60
-8	50	57
-9	165	173
-10	165	-168
-11	317	-313
-12	102	107
-13	73	-72

4,4,L

13	42	34
12	33	-35
11	67	-70
10	31	26
8	38	29
6	150	147
5	90	88
2	35	-27
1	171	163
0	351	-343
-1	429	-404
-3	194	195
-4	159	-158
-5	27	-18
-6	27	24
-7	38	33
-8	50	-47
-9	54	-52
-10	48	52
-11	26	-30
-12	125	125

4,3,L

13	33	24
12	35	-32
11	61	-61
10	23	25
9	60	56
8	100	-107
7	106	101
6	22	17
5	246	233
4	78	78
3	124	109
2	46	36
1	414	-382
0	428	443
-1	216	-212
-2	252	244
-3	25	-29
-4	294	-283
-5	406	-385
-6	220	212
-7	25	24
-8	25	30
-9	30	-26
-10	300	313
-11	358	358
-12	103	-106
-13	42	35

4,2,L

13	34	-22
10	39	-41
9	88	90
8	97	-95
7	103	104
5	156	176
4	187	-190
3	183	-184
2	22	29
1	105	-109
0	401	397
-1	323	-322
-2	463	-448
-3	128	-110
-4	206	-179
-5	151	148
-6	276	-258
-7	102	-102
-11	69	-67
-12	38	38
-13	24	-16

4,1,L

14	98	-77
13	30	-21
11	76	82
9	33	-15
8	70	78
7	125	-122
6	331	-307
5	175	-171
4	466	-468
3	257	-243
2	342	-340
1	235	-228
-1	490	509
-2	72	56
-3	17	16
-4	193	176
-5	95	88
-6	28	-29
-7	37	-39
-8	201	182
-10	323	-337
-11	169	-167
-12	108	104

4,0,L

10	69	-64
8	348	313
6	315	-283
4	667	679
2	338	337
0	74	71
-2	58	54
-4	795	822
-6	677	657
-8	77	-71
-10	31	-19
-12	230	-229
-14	35	-29

3,11,L

3	26	-29
-2	28	29

3,10,L

7	30	-25
6	35	28
5	57	57
3	51	-54
2	99	-108
-2	23	14
-3	28	27
-6	35	-33

3,9,L

8	38	43
5	39	-37
3	35	-32
2	43	43
1	29	-28
-5	32	-31
-6	39	-47
-10	42	39

3,8,L

6	66	-68
5	40	41
4	66	65
3	81	83
2	267	282
1	193	-188
0	24	25
-1	29	35
-4	100	-102
-5	47	-46
-6	96	96
-8	32	-29
-9	35	49
-10	53	49
-11	33	36

3,7,L

12	45	36
9	24	-22
8	51	-60
7	27	-27
6	34	30
5	28	36
4	186	182
3	28	25
2	38	36
1	23	16
0	56	52
-1	38	-33
-2	139	-133
-3	32	-37
-4	63	72
-7	63	-73
-11	66	-67
-12	72	69

3,6,L

10	65	-61
9	23	-23
8	68	-71
6	69	65
5	22	-15
4	25	34
3	75	-71
2	191	-185
1	159	149
-1	85	-81
-2	141	-136
-3	45	43
-4	63	64
-5	28	-26
-6	30	31
-8	35	-40
-9	29	30
-10	60	-63
-11	31	-35
-12	32	34

3,5,L

12	50	-41
11	34	-31
9	153	150
8	162	165
5	25	8
4	41	-38
3	176	-162
2	229	-226
1	227	-213
0	88	-93
-1	33	42
-2	237	-222
-3	124	111
-4	88	-88
-5	27	-3
-7	103	98
-10	87	-86
-12	168	-165
-13	28	27
-14	42	58

3,4,L

14	49	45
12	28	-26
11	58	59
10	77	85
9	39	39
8	245	245
7	69	-63
6	105	-97
5	191	-182
4	18	-13
2	155	-149
0	20	7
-1	147	119
-2	46	-41
-3	270	247
-4	276	253
-5	23	-39
-6	57	-67
-8	71	80
-10	99	108
-11	52	61
-14	26	25

3,3,L

13	68	61
12	38	33
10	49	50
9	227	-219
8	165	-163
7	105	91
6	33	30
5	58	43
4	71	67
2	95	95
1	215	194
0	134	143
-1	494	496
-2	496	504
-3	244	-223
-4	27	23
-5	138	114
-6	82	-79
-7	51	-58
-9	25	-37
-12	133	129
-13	127	-131

3,2,L

15	20	-25
14	25	-18
11	72	-77
9	49	-54
8	137	-148
7	227	224
6	306	-293
5	179	-182
4	57	43
3	426	-414
2	92	89
1	80	87
0	177	-125
-1	41	34
-2	51	-51
-3	37	26
-4	43	41
-5	105	98
-6	279	-269
-7	32	-13
-8	89	-92
-9	51	-47
-12	70	-69
-11	136	126
-12	26	28
-13	34	-45
-14	60	56
-15	32	28

3,1,L

15	44	[illegible]
13	77	[illegible]
11	61	55
10	39	-43
7	115	-119
6	96	-91
5	17	-19
4	92	-106
2	211	188
1	381	423
0	390	-430
-1	325	353
-2	155	148
-3	903	-928
-4	143	-137
-5	58	61
-6	74	68
-7	208	184
-8	42	41
-9	95	98
-10	82	81
-11	35	-44
-12	55	-58
-13	143	137

3,0,L

15	63	58
13	24	26
11	86	87
7	80	-66
5	585	499
1	440	-522
-1	21	15
-3	995	-1281
-5	248	241
-7	91	-94
-11	298	-293
-15	55	-44

2,11,L

4	27	-23
3	26	-27
2	37	39
1	32	37
-1	26	28
-2	39	39
-4	26	28
-5	26	-38
-6	25	-29

2,10,L

5	24	27
3	178	-188
2	186	-188
1	99	97
-7	39	38
-8	30	-31

2,9,L

0	46	48
5	46	-46
4	54	-52
3	67	69
2	108	-116
1	86	85
0	31	-34
-2	24	-28
-4	64	67
-6	26	22
-7	63	70

2,8,L

9	33	-32
7	126	113
4	89	86
3	318	333
2	31	25
1	258	-271
0	25	28
-1	48	-53
-3	28	-33
-4	43	49
-5	54	53
-6	44	-44
-9	77	-80

2,7,L

11	29	-28
8	117	-122
6	33	32
5	38	46
3	46	-45
2	182	193
1	113	-112
0	124	126
-1	151	156
-2	31	28
-3	104	-104
-4	89	-93
-5	54	55
-7	98	-107
-8	28	-33
-10	28	-28
-11	42	44
-13	30	-32

2,6,L

13	44	-38
12	27	25
7	98	-112
6	48	-38
5	22	-22
4	22	-25
3	21	-17
2	67	64
1	417	425
-3	194	-185
-4	73	64
-5	65	-58
-6	29	-24
-7	62	-65
-8	36	37
-9	105	107
-10	35	-34
-11	30	-29

2,5,L

12	38	36
11	23	-17
10	27	-12
9	95	103
7	47	51
6	53	-52
5	65	-68
4	21	-19
3	209	-219
2	250	-265
1	30	32
0	54	58
-1	341	-321
-2	246	237
-3	32	32
-4	38	-37
-5	101	143
-7	28	-24

Table 5.3.3 (cont'd)

2,5,L

-8	48	45
-10	24	15
-11	74	-73
-12	110	108
-13	120	121
-14	63	-65

2,4,L

13	56	60
12	87	-83
11	52	-48
9	68	66
8	72	-69
7	94	98
6	81	-72
5	242	-226
4	127	124
3	95	-87
2	156	-163
1	557	-582
0	53	-47
-1	27	36
-2	286	276
-3	456	449
-4	372	-338
-5	100	115
-7	50	38
-8	44	40
-9	42	-37
-10	43	36
-11	124	128
-12	47	-52
-13	29	-29
-14	76	-75
-15	58	-60

2,3,L

14	26	14
12	25	-27
11	35	-37
9	109	-114
8	207	208
6	178	178
5	35	42
3	135	120
2	221	-210
0	469	-476
-1	46	31
-2	289	-283
-3	18	-16
-4	214	-216
-5	19	27
-6	138	124
-10	37	32
-11	51	59
-12	245	-247
-13	140	-144
-14	43	44
-15	26	-32

2,2,L

15	55	-53
13	112	-111
12	67	70
11	68	66
10	35	-38
9	98	-93
8	154	-135
7	77	-88
6	408	389
5	92	71
4	92	-95
3	73	60
1	415	446
0	191	-180
-1	81	75
-2	320	-330
-3	335	-348
-4	91	72
-5	200	184
-6	166	149
-7	70	-68
-8	101	98
-10	67	-51
-11	53	-53
-12	60	63
-13	96	90
-14	42	41
-15	39	36

2,1,L

14	37	-31
13	28	-24
12	91	90
11	84	79
10	65	-58
9	20	30
8	136	-114
7	101	-87
6	95	-99
5	150	122
4	704	700
3	256	248
2	953	1036
1	16	25
0	185	-199
-1	46	68
-2	676	761
-3	445	476
-4	249	-252
-5	385	-370
-6	74	71
-7	143	127
-8	403	-377
-9	22	17
-10	126	-117
-12	89	85
-14	49	45
-16	46	38

2,0,L

16	32	-17
14	52	49
12	53	-52
8	403	387
6	435	-401
4	931	-873
0	286	311
-2	88	-78
-4	128	133
-6	172	-155
-8	447	-431
-10	74	58

1,11,L

5	31	24
4	37	-39
3	30	-33
2	41	45
1	61	65
-1	28	-31
-2	38	44
-4	40	-44
-5	33	-32

1,10,L

7	62	-61
6	29	29
4	60	-61
3	37	-39
0	67	70
-1	45	45
-2	40	-39
-3	44	45
-4	49	51

1,9,L

8	28	25
7	30	31
5	25	-26
4	35	35
3	30	32
2	35	31
1	51	-61
-1	73	70
-2	94	-100
-6	46	42
-9	31	31

1,8,L

11	25	19
10	30	-33
8	26	23
7	30	33
6	74	-77
5	35	37
4	103	114
3	115	114
2	130	-127
1	195	-205
0	203	-206
-1	47	-47
-3	43	-41
-4	87	-94
-5	53	50
-6	58	60
-8	49	-54
-9	31	31
-11	26	-24

1,7,L

10	62	-55
6	146	146
4	85	-79
3	82	74
2	22	-14
1	164	167
0	116	-106
-1	50	-41
-2	25	22
-3	49	46
-4	81	-88
-5	27	-33
-6	94	95
-7	41	-40
-8	25	-27
-10	28	25
-11	33	-27
-13	45	43

1,6,L

11	37	-34
10	34	26
7	59	58
6	180	186
5	88	-82
4	103	-96
3	69	73
2	212	203
1	118	116
0	140	135
-2	31	34
-3	76	60
-4	82	80
-5	86	-90
-6	94	94
-8	86	-87
-9	44	43
-13	38	-33
-14	55	53

1,5,L

14	33	-30
12	69	-69
9	83	85
8	105	93
7	117	-106
6	471	-458
5	35	48
4	27	38
3	299	-282
2	277	-267
1	99	97
0	679	688
-1	111	-107
-2	140	129
-3	263	248
-4	307	295
-5	184	-173
-6	162	-150
-7	112	110
-8	69	64
-9	44	-50
-10	23	21
-13	98	-93
-14	52	52

1,4,L

15	14	26
12	43	-38
11	81	78
10	56	50
9	194	-190
8	45	36
7	33	-27
6	240	-226
5	187	175
4	224	-209
3	84	-82
2	169	-173
1	194	173
0	315	-314
-1	28	2
-2	34	-66
-3	255	-232
-4	38	-24
-6	145	-86
-7	46	51
-8	142	141
-9	143	-145
-11	53	51
-14	130	-125
-15	44	44

1,3,L

15	61	59
14	27	29
12	45	50
10	86	90
9	117	-122
8	144	-114
7	338	301
6	358	340
5	145	-135
4	40	41
3	188	177
2	332	299
1	957	-1008
0	1071	-1079
-1	530	568
-3	458	-437
-4	264	-272
-5	87	75
-6	127	85
-7	51	38
-8	70	-64
-13	63	65
-14	38	45
-15	45	51

1,2,L

15	39	-35
14	39	39
13	61	58
11	64	59
10	34	-40
9	93	86
8	126	-121
7	155	154
6	94	114
5	313	-308
4	167	144
3	57	-39
1	194	186
0	243	234
-1	309	-311
-2	28	-25
-3	252	254
-4	35	46
-5	17	-19
-6	55	-65
-7	109	-110
-8	117	-113
-10	120	124
-11	37	-36
-12	50	50
-14	51	45

1,1,L

11	73	70
10	23	-24
9	115	-102
7	329	-303
5	438	414
4	98	106
3	117	-111
2	28	27
1	69	-74
0	228	224
-1	619	-568
-2	198	-204
-3	67	-66
-4	178	177
-5	173	-162
-6	112	-103
-7	114	104
-8	68	70
-9	145	-150
-10	40	-34
-11	39	-44
-13	29	24
-14	75	-75

1,0,L

13	121	-119
11	265	-258
9	35	-29
7	381	-382
5	512	486
3	1024	-998
1	216	216
-3	29	-12
-5	151	156
-7	231	248
-9	210	187
-11	37	23
-13	39	38

0,11,L

3	29	-26
2	36	38
1	54	38

0,10,L

7	31	-26
6	27	-24
4	26	29
3	48	-51
1	100	104
0	140	148

0,9,L

9	56	-51
8	32	36
7	26	26
4	58	-57
3	47	43
2	48	-54
1	139	-146

0,8,L

12	45	47
11	49	-48
7	93	91
6	60	64
5	142	-146
4	22	-26
3	24	21
2	65	-67
1	379	-397
0	203	-209

0,7,L

10	48	43
9	51	52
8	69	-72
6	29	28
4	93	88
3	68	-74
2	108	97
1	115	107

0,6,L

12	24	-22
10	46	-48
7	98	-94
0	149	-137
5	61	65
4	38	-22
3	47	-46
2	277	279
1	674	705
0	25	16

0,5,L

14	40	36
12	24	-21
9	69	-66
8	81	-84
7	153	-144
6	125	117
5	47	-53
4	174	157
3	110	84
2	78	-64
1	401	418

0,4,L

11	90	-89
10	60	59
9	38	32
8	69	67
7	79	75
6	142	126
5	95	101
4	101	102
3	75	82
2	353	-332
1	485	-395
0	150	159

0,3,L

15	35	35
14	54	-55
13	33	32
11	47	51
10	35	41
9	52	53
8	38	36
7	214	209
6	147	-139
5	238	258
4	493	-504
3	267	-236
2	375	-378
1	818	-765

0,2,L

12	59	60
11	133	136
10	67	-66
9	66	79
8	25	-27
7	160	-140
6	378	347
5	159	138
4	253	-220
3	345	-321
2	110	-109
1	761	687

0,1,L

12	23	-18
11	58	-52
10	176	-170
9	19	22
8	89	84
7	191	-188
6	66	71
5	161	-170
4	144	142
3	349	336
2	215	-214

0,0,L

14	43	-42
10	46	42
8	50	45
6	718	-742
4	408	399
2	215	-247

Table 6.3.4.

Bond lengths (Å) with standard deviations in parentheses.

N(1) - O(1)	1.231(8)	N(3) - O(2)	1.185(11)
C(1) - N(1)	1.432(9)	C(11) - N(3)	1.463(9)
C(1) - C(2)	1.399(7)	C(11) - C(12)	1.369(7)
C(2) - C(3)	1.378(7)	C(12) - C(13)	1.367(7)
C(3) - C(4)	1.391(6)	C(13) - C(14)	1.420(6)
C(4) - C(5)	1.429(5)	C(14) - C(15)	1.411(6)
C(5) - C(6)	1.376(6)	C(15) - C(16)	1.375(6)
C(6) - C(1)	1.371(7)	C(16) - C(11)	1.398(7)
C(4) - N(2)	1.351(5)	C(14) - N(4)	1.346(5)
N(2) - C(7)	1.462(6)	N(4) - C(17)	1.462(6)
C(7) - C(8)	1.522(8)	C(17) - C(18)	1.503(8)
N(2) - C(9)	1.472(5)	N(4) - C(19)	1.465(6)
C(9) - C(10)	1.506(7)	C(19) - C(20)	1.499(7)
H(1) - C(2)	0.86(5)	H(15) - C(12)	1.01(6)
H(2) - C(3)	1.03(6)	H(16) - C(13)	0.99(6)
H(3) - C(5)	0.79(6)	H(17) - C(15)	0.98(6)
H(4) - C(6)	0.97(5)	H(18) - C(16)	0.93(6)
H(5) - C(7)	1.01(6)	H(19) - C(17)	0.88(6)
H(6) - C(7)	1.04(6)	H(20) - C(17)	1.03(6)
H(7) - C(8)	0.84(7)	H(21) - C(18)	0.99(7)

Table 6.3.4. (cont'd)

H(8) - C(8)	1.00(7)	H(22) - C(18)	0.94(7)
H(9) - C(8)	1.00(7)	H(23) - C(18)	1.05(7)
H(10) - C(9)	0.93(6)	H(24) - C(19)	0.92(6)
H(11) - C(9)	0.96(6)	H(25) - C(19)	0.98(6)
H(12) - C(10)	1.08(7)	H(26) - C(20)	0.92(7)
H(13) - C(10)	1.05(6)	H(27) - C(20)	1.14(7)
H(14) - C(10)	0.85(7)	H(18) - C(20)	0.97(7)

Table 6.3.5.

Bond angles (degrees) with standard deviations in parentheses.

C(1)-N(1)-O(1)	111.3(0.6)	C(11)-N(3) -O(2)	109.9(0.8)
C(2)-C(1)-N(1)	113.1(0.4)	C(12)-C(11)-N(3)	113.3(0.5)
C(6)-C(1)-N(1)	127.6(0.5)	C(16)-C(11)-N(3)	127.2(0.5)
C(6)-C(1)-C(2)	119.4(0.4)	C(16)-C(11)-C(12)	119.5(0.4)
C(1)-C(2)-C(3)	119.5(0.4)	C(11)-C(12)-C(13)	121.5(0.5)
C(2)-C(3)-C(4)	122.0(0.4)	C(12)-C(13)-C(14)	120.6(0.4)
C(3)-C(4)-C(5)	117.7(0.4)	C(13)-C(14)-C(15)	117.4(0.4)
C(4)-C(5)-C(6)	119.3(0.4)	C(14)-C(15)-C(16)	120.7(0.4)
C(5)-C(6)-C(1)	122.1(0.4)	C915)-C(16)-C(11)	120.4(0.4)
C(3)-C(4)-N(2)	122.2(0.4)	C(13)-C(14)-N(4)	120.1(0.4)
C(5)-C(4)-N(2)	120.2(0.4)	C(15)-C(14)-N(4)	121.8(0.4)
C(4)-N(2)-C(7)	122.6(0.4)	C(14)-N(4) -C(17)	121.7(0.4)
C(4)-N(2)-C(9)	121.7(0.4)	C(14)-N(4) -C(19)	122.5(0.3)
N(2)-C(7)-C(8)	112.7(0.4)	N(4) -C(17)-C(18)	113.0(0.4)
N(2)-C(9)-C(10)	112.5(0.4)	N(4) -C(19)-C(20)	112.8(0.4)
C(7)-N(2)-C(9)	115.7(0.4)	C(17)-N(4) -C(19)	115.8(0.4)
C(1)-C(2)-H(1)	108(4)	C(11)-C(12)-H(15)	115(3)
C(3)-C(2)-H(1)	133(4)	C(13)-C(12)-H(15)	123(3)
C(2)-C(3)-H(2)	112(3)	C(12)-C(13)-H(16)	120(3)
C(4)-C(3)-H(2)	126(3)	C(14)-C(13)-H(16)	119(3)
C(4)-C(5)-H(3)	116(4)	C(14)-C(15)-H(17)	119(3)
C(6)-C(5)-H(3)	124(4)	C(16)-C(15)-H(17)	120(3)

Table 6.3.5. (cont'd)

C(5) -C(6) -H(4)	113(3)	C(15)-C(16)-H(18)	116(3)
C(1) -C(6) -H(4)	125(3)	C(11)-C(16)-H(18)	123(3)
N(2) -C(7) -H(5)	113(3)	N(4) -C(17)-H(19)	108(4)
C(8) -C(7) -H(5)	111(4)	C(18)-C(17)-H(19)	97(4)
N(2) -C(7) -H(6)	114(3)	N(4) -C(17)-H(20)	108(3)
C(8) -C(7) -H(6)	104(3)	C(18)-C(17)-H(20)	116(3)
H(5) -C(7) -H(6)	101(5)	H(19)-C(17)-H(20)	114(5)
C(7) -C(8) -H(7)	107(5)	C(17)-C(18)-H(21)	119(4)
C(7) -C(8) -H(8)	107(4)	C(17)-C(18)-H(22)	109(4)
C(7) -C(8) -H(9)	110(4)	C(17)-C(18)-H(23)	116(4)
H(7) -C(8) -H(8)	128(6)	H(21)-C(18)-H(22)	100(6)
H(7) -C(8) -H(9)	105(6)	H(21)-C(18)-H(23)	110(5)
H(8) -C(8) -H(9)	96(5)	H(22)-C(18)-H(23)	100(6)
N(2) -C(9) -H(10)	109(4)	N(4) -C(19)-H(24)	109(4)
C(10)-C(9) -H(10)	115(4)	C(20)-C(19)-H(24)	110(4)
N(2) -C(9) -H(11)	105(4)	N(4) -C(19)-H(25)	109(4)
C(10)-C(9) -H(11)	115(4)	C(20)-C(19)-H(25)	112(3)
H(10)-C(9) -H(11)	106(5)	H(24)-C(19)-H(25)	102(5)
C(9) -C(10)-H(12)	109(4)	C(19)-C(20)-H(26)	121(4)
C(9) -C(10)-H(13)	106(4)	C(19)-C(20)-H(27)	108(3)
C(9) -C(10)-H(14)	116(5)	C(19)-C(20)-H(28)	102(4)
H(12)-C(10)-H(13)	104(5)	H(26)-C(20)-H(27)	98(5)
H(12)-C(10)-H(14)	107(6)	H(26)-C(20)-H(28)	110(6)
H(13)-C(10)-H(14)	114(6)	H(27)-C(20)-H(2')	118(5)

Table 6.3.6.

Torsion angles* (degrees) in the diethylamino groups.

Atom A	Atom B	Atom C	Atom D	Angle
C(4)	N(2)	C(7)	C(8)	85.4
C(4)	N(2)	C(9)	C(10)	89.7
C(14)	N(4)	C(17)	C(18)	87.1
C(14)	N(4)	C(19)	C(20)	86.0

*The angle A-B-C-D is defined as positive if when viewed along the B-C bond atom A has to be rotated in a clockwise direction to eclipse atom D.

Table 6.3.7.

Closest intermolecular contacts (Å) with standard deviations in parenthesis. Only C ••• C contacts less than 3.8 Å and C ••• O contacts less than 3.6 Å have been included.

Equivalent positions other than x, y, z required to describe these intermolecular contacts are :

1. $-x, -y, -z$
2. $1-x, 1-y, 1-z$
3. $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
4. $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
5. $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
6. $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
7. $\frac{3}{2}-x, \frac{3}{2}+y, \frac{3}{2}-z$
8. $\frac{3}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$

Atom 1	Atom 2	Distance
O(1)	$C(7)^4$	3.569(8)
O(1)	$C(8)^2$	3.432(9)
O(1)	$C(18)^3$	3.556(8)
O(2)	$C(8)^6$	3.560(10)
O(2)	$C(17)^5$	3.557(9)
O(2)	$C(19)^5$	3.594(9)

Atom 1	Atom 2	Distance
C(1)	$C(15)^7$	3.774(6)
C(3)	$C(20)^7$	3.607(7)
C(4)	$C(18)^8$	3.677(6)
C(4)	$C(19)^7$	3.710(7)
C(5)	$C(15)^1$	3.751(6)
C(6)	$C(14)^1$	3.763(6)
C(12)	$C(20)^7$	3.740(7)

Table 6.3.8.

Mean planes, referred to orthogonal co-ordinates X', Y and Z' (where X' = $\underline{a}\underline{x}\sin\beta$, Y = $\underline{b}\underline{y}$, Z' = $\underline{a}\underline{x}$ + $\underline{c}\underline{z}\cos\beta$), displacements of the atoms from the planes (Å) and angles between the planes (degrees).

Plane 1 : $-0.0987X' + 0.9856Y - 0.1373Z' = 1.6830$ Å

Atoms in plane		
C(1)	-0.0080	
C(2)	0.0054	
C(3)	-0.0021	
C(4)	0.0013	
C(5)	-0.0039	
C(6)	0.0074	r.m.s. distance from plane = 0.005 Å

Plane 2 : $-0.0281X' + 0.9972Y - 0.0694Z' = 2.4909$ Å

N(2)	0.0018	
C(4)	-0.0003	
C(7)	-0.0008	
C(9)	-0.0008	r.m.s. distance from plane = 0.001 Å

Table 6.3.8. (cont'd)

Plane 3 : $-0.6523X - 0.1277Y - 0.7471Z' = -3.0148$ Å

C(11)	0.0084	
C(12)	-0.0128	
C(13)	0.0099	
C(14)	-0.0030	
C(15)	-0.0011	
C(16)	-0.0015	r.m.s. distance from plane = 0.008 Å

Plane 4 : $-0.6525X' - 0.0960Y - 0.7513Z' = -2.9334$ Å

N(4)	-0.0121	
C(14)	0.0025	
C(17)	0.0049	
C(19)	0.0047	r.m.s. distance from plane = 0.007 Å

Plane 5 : $-0.0911X' + 0.9864Y - 0.1367Z' = 1.7223$ Å

Atoms in plane : C(1), N(1), O(1)

Plane 6 : $-0.6519X' - 0.0352Y - 0.7575Z' = -2.7345$ Å

Atoms in plane : C(9), N(3), O(2).

Table 6.3.8. (cont'd)

Interplanar angles

Angle $1 \wedge 2 = 6.0^{\circ}$

Angle $3 \wedge 4 = 2.4^{\circ}$

Angle $1 \wedge 5 = 0.4^{\circ}$

Angle $3 \wedge 6 = 5.3^{\circ}$

Angle $1 \wedge 3 = 87.6^{\circ}$

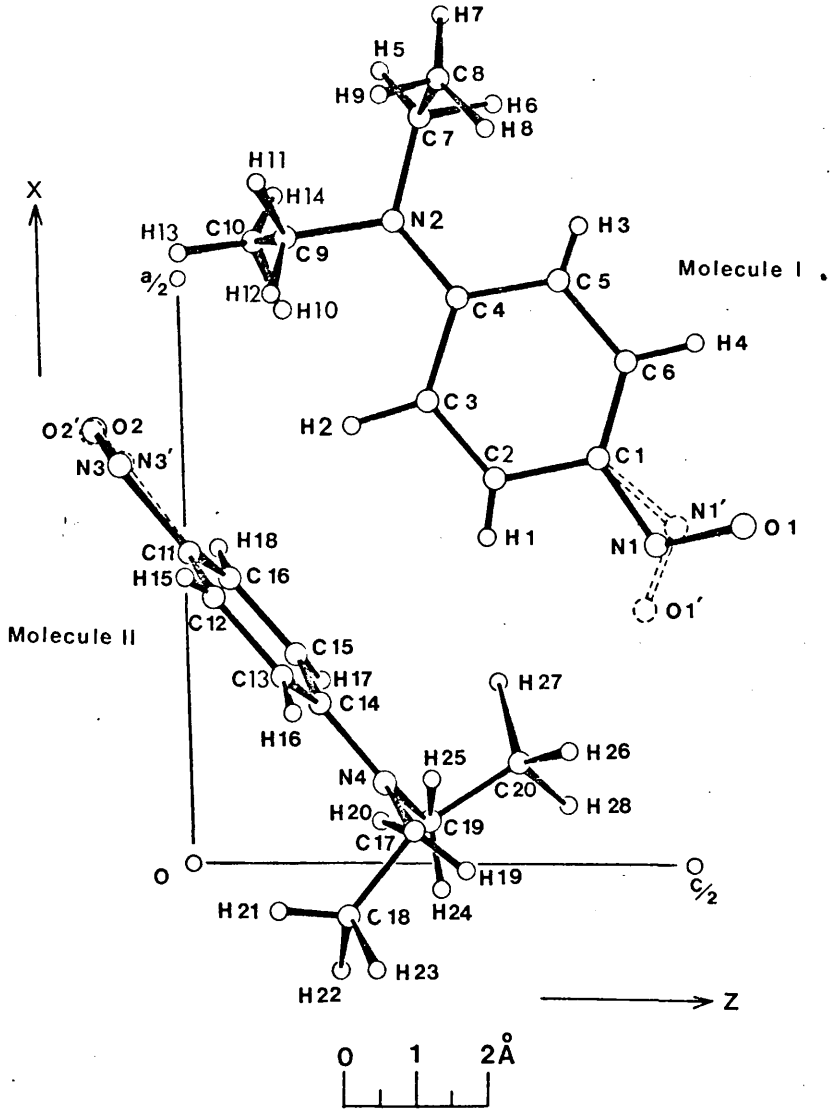


Figure 6.3.1 : The two molecules of N,N-diethyl p-nitrosoaniline in the asymmetric unit, showing the atomic numbering system employed.

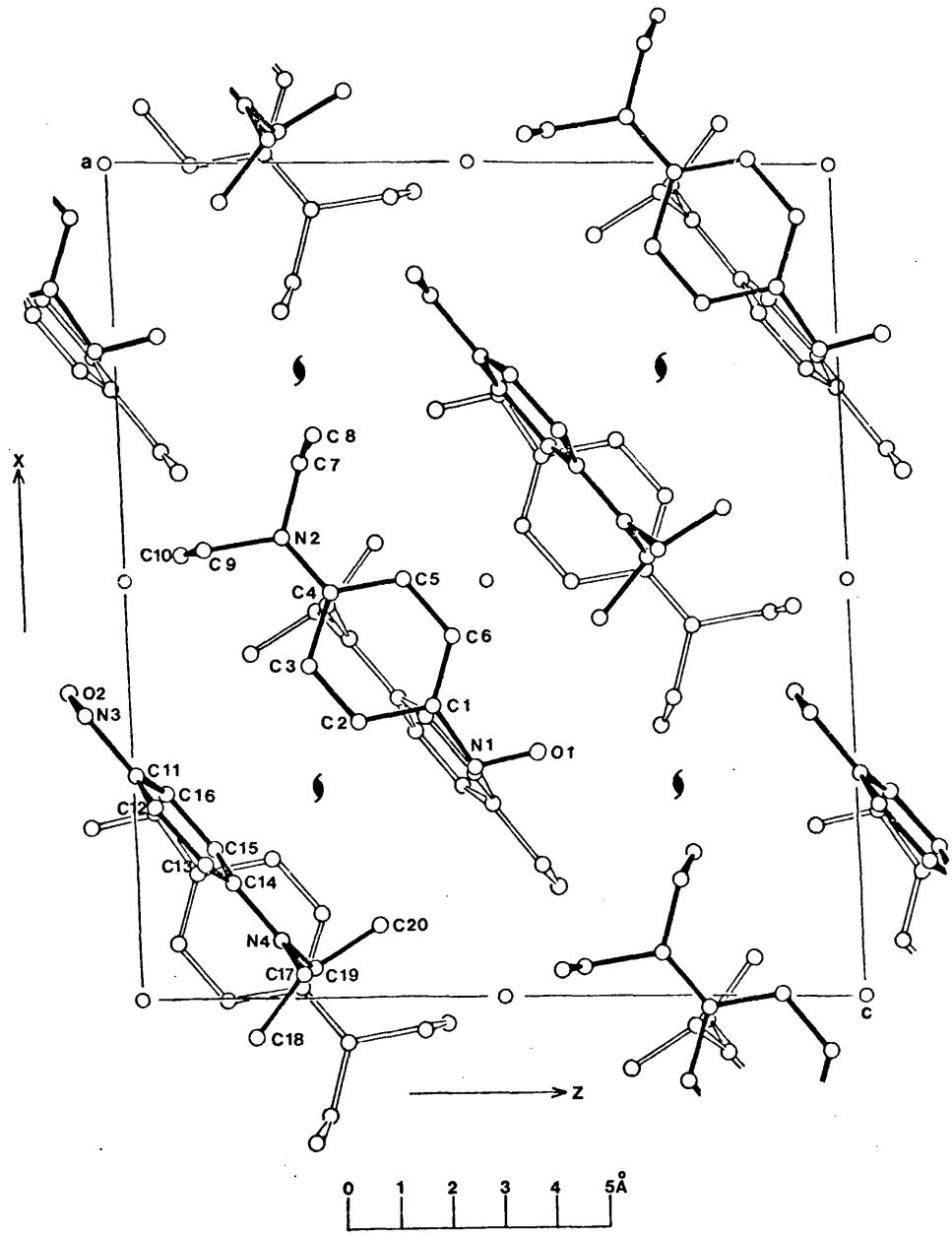


Figure 6.3.2 : The molecular packing of N,N-diethyl p-nitrosoaniline projected along the b axis, from y = $\frac{1}{2}$ to y = $-\frac{1}{2}$. The hydrogen atoms have been omitted for clarity.

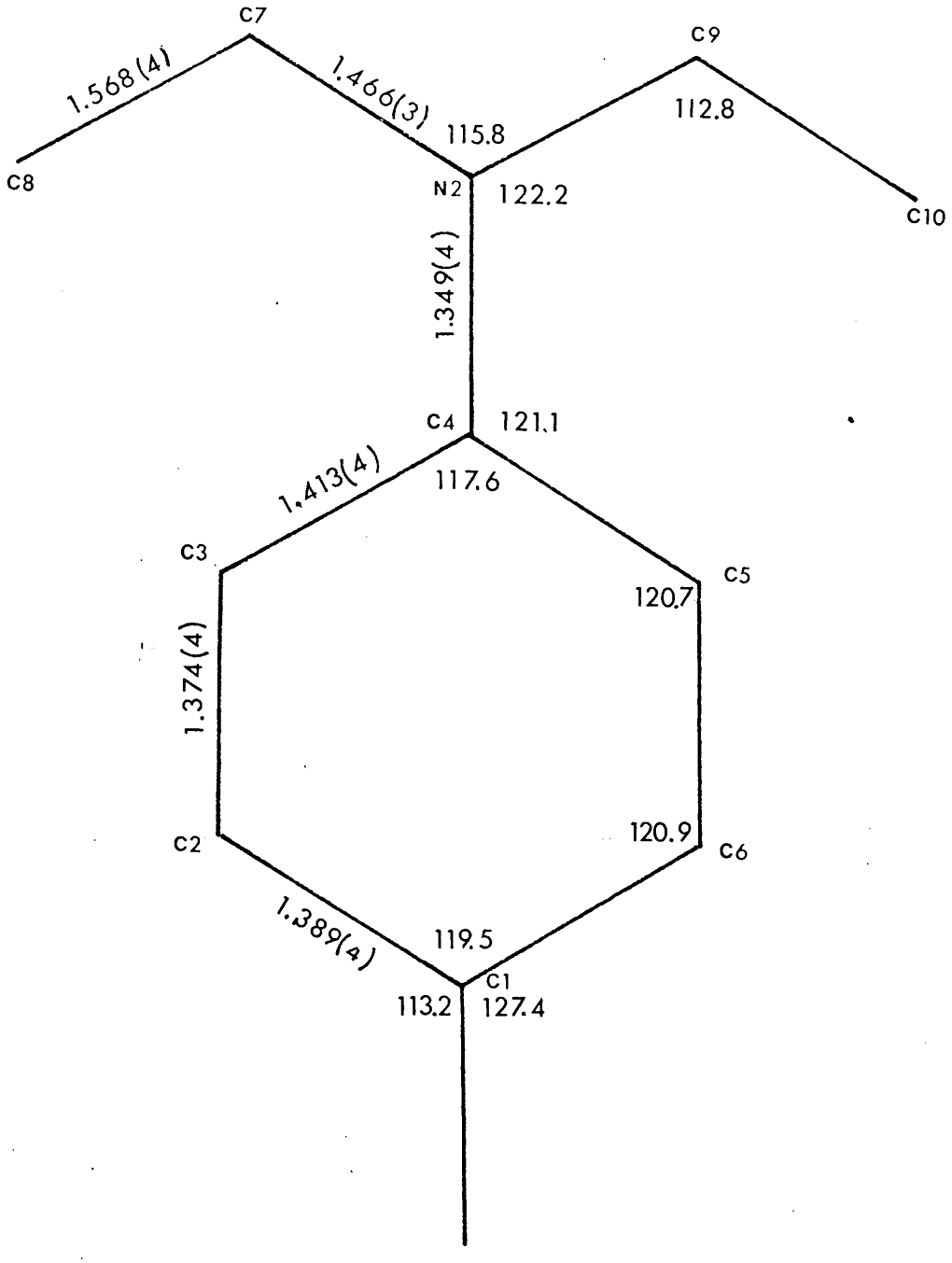


Figure 6.3.3: Mean bond lengths/angles of the N,N-diethyl aniline residues.